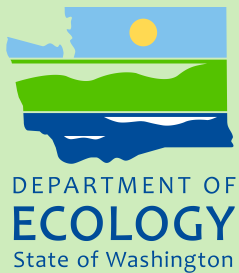


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Spokane River PCB Source Assessment 2003-2007



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Spokane River PCB Source Assessment 2003-2007

by

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Environmental Assessment Program
Washington State Department of Ecology
Olympia, Washington 98504-7710

Waterbody Numbers:

WA-57-1010: Middle Spokane River
WA-54-1010, WA-54-1020: Lower Spokane River
WA-54-9040: Lake Spokane (formerly Long Lake-Spokane River)
WA-55-1010: Little Spokane River

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Abstract

The Spokane River does not meet Washington State human health criteria for polychlorinated biphenyls (PCBs) in edible fish tissue. During 2003 to 2007, the Department of Ecology conducted a series of water quality studies in an effort to assess sources of these legacy pollutants to the river. PCBs were analyzed in river water, industrial and municipal wastewater effluents, stormwater, suspended particulate matter, bottom sediments, sediment cores, and fish tissue. The study area covered the Spokane River from the Idaho border (river mile 96.1) to the mouth at the Columbia River. The lower part of the river flows through the Spokane Tribe of Indians reservation.

Total PCB concentrations in water increased with successive reaches moving downstream from the Idaho border (106 pg/l, parts per quadrillion) to lower Lake Spokane (formerly Long Lake; 399 pg/l), with a corresponding eight-fold increase in loads (477 – 3,664 mg/day), on average. The Washington State PCB human health criterion for surface water is 170 pg/l. Although PCB concentrations in Spokane River fish are generally much lower than historical levels, fish in most areas did not meet the state's human health criterion in edible tissue (5.3 ng/g, parts per billion).

Overall, PCB loading to Washington reaches of the river can be divided into the following source categories; City of Spokane stormwater (44%), municipal and industrial discharges (20%), and Little Spokane River (6%). In addition, PCB loading from Idaho at the state line represented 30% of the overall loading.

A PCB loading scenario was proposed to meet the Spokane Tribe human health water quality criterion for total PCBs (3.37 pg/l, equivalent to 0.1 ng/g in tissue). The scenario requires a 95% PCB load reduction at the Idaho border, a 97% load reduction in the Little Spokane River, and ≥99% reductions in municipal, industrial, and stormwater discharges. A food web bioaccumulation model indicated that PCB loads in water and PCB concentrations in sediment would require large reductions to meet the Spokane Tribe criterion.

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Executive Summary

Section 303(d) of the federal Clean Water Act requires states to prepare a list every two years of waterbodies that do not meet water quality standards. In Washington, the 303(d) list is compiled by the Washington State Department of Ecology (Ecology). The Clean Water Act requires that waterbodies on the 303(d) list be cleaned up by pollution-control programs or that a Total Maximum Daily Load (TMDL) be developed for the pollutants of concern. A TMDL determines the amount of pollutant that can be discharged to a waterbody and still meet standards (loading capacity) and allocates that load among the various sources.”

Fifteen waterbody segments of the Spokane River and Lake Spokane (also known as Long Lake), and one segment of the Little Spokane River are on the 2008 303(d) list for not meeting (exceeding) Washington State’s human health water quality criterion for polychlorinated biphenyls (PCBs) in edible fish tissue (Table ES-1). PCBs are legacy pollutants no longer produced or no longer put into new use in the United States. PCBs had numerous industrial applications as insulating fluids, plasticizers, in inks, and carbonless paper, and as heat transfer and hydraulic fluids. Environmental Protection Agency (EPA) has classified these compounds as probable human carcinogens.

Table ES-1. 303(d) Listings for Total PCBs in the Spokane River.

Waterbody	Reach	Waterbody Number	Watercourse Number	Listing ID
Spokane River	Idaho Border to Latah Creek	WA-57-1010	QZ45UE	14397 14398 8201 8207 8202 14402
Spokane River	Latah Creek to Ninemile Dam	WA-54-1010	QZ45UE	14400 14385 9033
Little Spokane River	Near mouth	WA-55-1010	JZ70CP	9051
Lake Spokane (Long Lake)	Ninemile Dam to Lake Spokane Dam	WA-54-9040	QZ45UE	9021 36441 9015 36440
Spokane River	Lake Spokane Dam to Mouth	WA-54-1020	QZ45UE	9027

Ecology conducted the water quality studies described in this report from 2003 to 2007 to assess PCB sources to the Spokane River. The goal of these efforts was to quantify PCB contamination and identify necessary reductions in sources and the receiving waters to meet applicable PCB water quality criteria in the Spokane River. The studies analyzed PCBs in river water, industrial and municipal effluents, stormwater, suspended particulate matter, bottom sediments, sediment cores, and fish tissue.

The Spokane River, shown in Figure ES-1, begins in northern Idaho at the outlet of Lake Coeur d'Alene and flows west 112 miles to the Columbia River (Lake Roosevelt). The study area covered the Spokane River from the Idaho border (river mile 96.1) to the Columbia. The watershed encompasses over 6,000 square miles (15,500 km²) in Washington and Idaho. The river flows through the smaller cities of Post Falls and Coeur d'Alene in Idaho and large urban areas of the Spokane Valley and Spokane in Washington. Other cities in the watershed include Liberty Lake, Deer Park, and Medical Lake Washington as well as Wallace and Kellogg Idaho upstream from Lake Coeur d'Alene. The Spokane Tribe of Indians reservation lies along the north bank of the lower river (Spokane Arm of Lake Roosevelt).

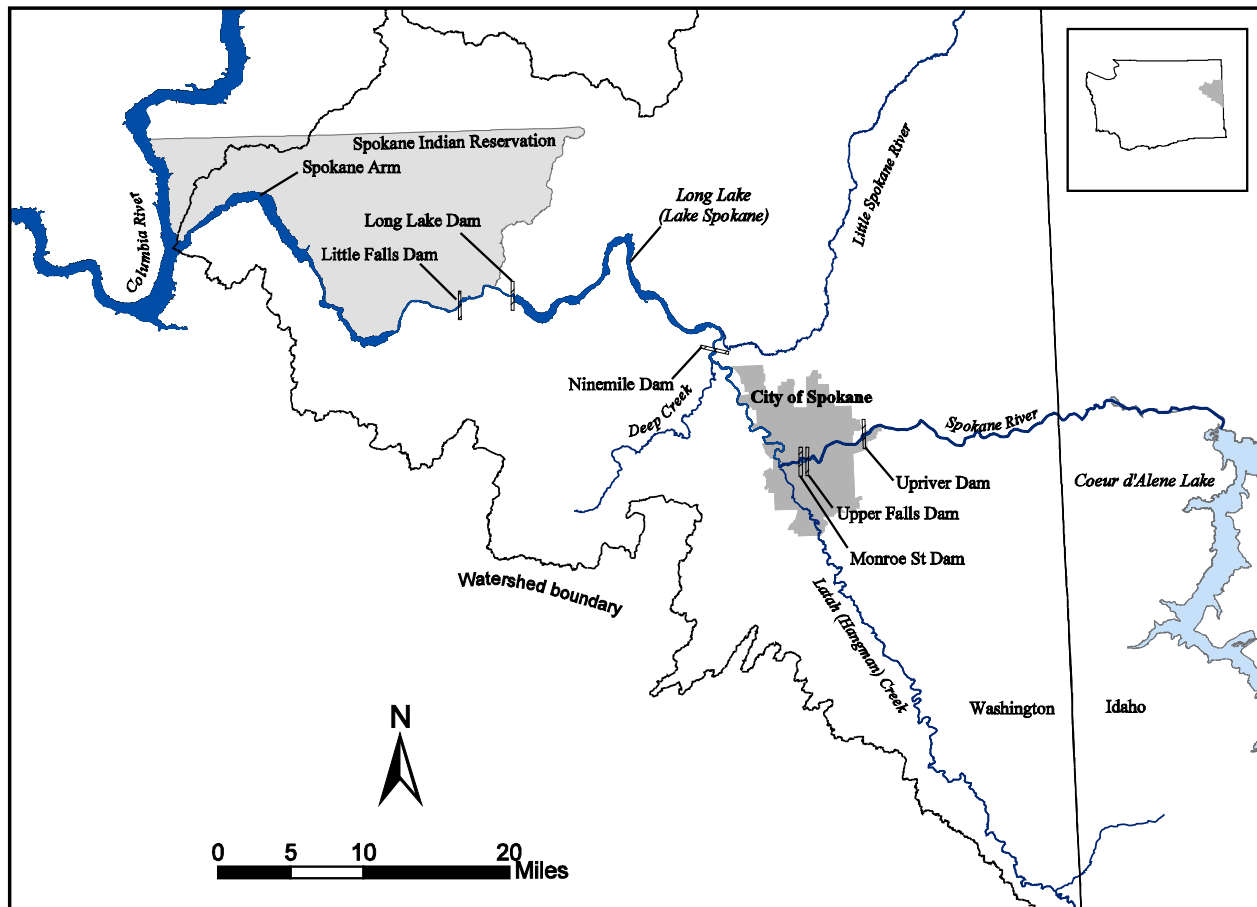


Figure ES-1: Spokane River Basin.

The Spokane Tribe human health PCB water quality criterion of 3.37 pg/l (parts per quadrillion) was used as the basis for calculating necessary PCB load reductions. The criterion is equivalent to 0.1 ng/g (parts per billion) in edible fish tissue. Although this criterion only applies to the Spokane Arm and lower half of the Little Falls reservoir, it cannot reasonably be met within these bounds unless PCB concentrations in upstream reaches are reduced to levels near the criterion. Washington State's human health criteria for PCBs is 170 pg/l (5.3 ng/g in fish tissue), the difference primarily being due to assumptions about human consumption rates of fish.

A PCB loading scenario is proposed to meet the Spokane Tribe human health criterion. The scenario requires a 95% PCB load reduction at the Idaho border, a 97% load reduction in the Little Spokane River, and $\geq 99\%$ reductions in municipal, industrial, and stormwater discharges. Based on the loads estimated in this report, the largest current contributor of PCBs to the river (44%) is the City of Spokane's partially combined sewer-stormwater system. This is the most important source to reduce.

A food web bioaccumulation model used to predict PCB concentrations in fish tissue from the levels in water and sediments indicates that reductions of $\geq 99\%$ would be required to meet the Spokane Tribe's fish tissue criterion where the Spokane River enters the reservation. Even with large reductions in PCBs, it seems unlikely that the Spokane tribal target (0.1 ng/g) in fish tissue is achievable. This concentration is approximately an order of magnitude lower than the median level (1.4 ng/g) reported in fish tissue from background areas of Washington in a 2010 statewide study conducted by Ecology (Johnson et al., 2010). Despite the extremely low tribal criteria, it is clear that further reductions in PCB loading are achievable. Implementing an adaptive management narrative limit in National Pollutant Discharge Elimination System (NPDES) permits might be a productive approach to establish a set of achievable targets for toxic chemical reductions.

Recommendations

Even though significant reductions in PCB levels have been measured in the Spokane River over the last two decades, achieving further reductions in PCBs will be a challenging long-term process which will require a strategy that uses a combination of activities to achieve water quality targets. To start meeting this challenge, Ecology has drafted a long-term strategy for reducing PCBs and other toxic chemicals in the Spokane River watershed.

The Spokane River Toxics Reduction Strategy requires coordination across several Ecology programs, including the Spokane River Urban Waters Program (UWP) which was formed in 2007. The primary purpose of this program is to identify and eliminate toxic chemicals at their source. The UWP also works cooperatively with local governments including the City of Spokane and the Spokane Regional Health District.

Under the reduction strategy, source identification and control will largely be carried out by the UWP. The strategy uses a three-pronged approach (prevention, management, and cleanup) to reduce sources. Priority is placed on using a systematic step-wise process for identifying potential PCB sources within a conveyance system, then reducing and/or eliminating sources as they are located.

The conceptual approach to reduce PCBs discharged to the Spokane River should continue to focus on:

1. Identifying PCB sources and reducing or eliminating them from stormwater and wastewater effluents.
2. Examining treatment alternatives for effluent PCB removal.
3. Implementing necessary treatment plant controls.
4. Characterizing PCB transport through groundwater.

Implementation of an adaptive management approach using narrative limits in NPDES permits should be explored as an option to establish a set of achievable targets for toxic chemical reductions. In addition, source reduction efforts should be coupled with an ongoing effectiveness monitoring program to evaluate progress in reaching water quality targets.

The 303(d) List

The federal Clean Water Act established a process to identify and clean up polluted waters. The Clean Water Act requires each state to have its own water quality standards designed to protect, restore, and preserve water quality. Water quality standards include (1) designated uses for aquatic life, recreation, water supply, and harvesting (fish consumption) and (2) criteria, usually numeric criteria, to protect those uses.

Every two years, states are required to prepare a list of waterbodies – lakes, rivers, streams, or marine waters – that do not meet water quality standards. This list is called the 303(d) list and is prepared by the Washington State Department of Ecology (Ecology). To develop the list, Ecology compiles its own ambient water quality data along with data from local, state, and federal governments, tribes, industries, and citizen monitoring groups. All data are reviewed to ensure that they were collected using appropriate scientific methods before being used to develop the 303(d) list. The 303(d) list is part of the larger Water Quality Assessment (www.ecy.wa.gov/programs/wq/303d/index.html).

The last comprehensive freshwater and marine water 303(d) list for Washington was prepared in 2008. Listing updates are now staggered, with the marine list completed in 2010 and the freshwater list scheduled to be completed in 2012. The next opportunity to evaluate compliance with water quality standards in the Spokane River will be in 2012.

The Clean Water Act requires that waterbodies on the 303(d) list be cleaned up by pollution-control programs or that a TMDL be developed. A pollution-control program needs to address the sources of pollution and have a monitoring and enforcement component. A TMDL identifies pollution problems in the watershed and specifies how much pollution needs to be reduced or eliminated to achieve clean water. When developing a pollution-control program or a TMDL, Ecology works with the local communities and other relevant stakeholders to identify all actions that need to occur to address the sources of pollution. A monitoring plan to assess the effectiveness of those implementation actions is also developed. That monitoring plan is used to determine success or the next steps needed.

Spokane River PCB Listings

The Spokane River begins in northern Idaho at the outlet of Lake Coeur d'Alene and flows west 112 miles to the Columbia River. Within Washington this includes Water Resource Inventory Areas (WRIAs) 54, 55, 56, and 57 (Figure 1). The designated uses for this area include aquatic life uses, recreation, fish consumption, and Spokane Tribe of Indians ceremonial, spiritual, and cultural uses (see *Water Quality Standards and Designated Uses* section).

Elevated levels of polychlorinated biphenyls (PCBs) are found in Spokane River water, sediments, fish tissue, and effluents being discharged to the river. Ecology first documented PCB contamination in Spokane River fish in the early 1980s (Hopkins et al., 1985), and numerous investigations have evaluated the extent of the contamination (e.g., Ecology, 1995; Johnson, 1997; Johnson, 2001; Anchor, 2004). One location behind Upriver Dam required clean-up of PCBs in bottom sediments under the Model Toxics Control Act (MTCA, WAC 173-340). Cleanup was completed in January 2007, and long-term monitoring for PCBs at this site began in the fall of 2008.

Most of the Spokane River fish analyzed for PCBs fail to meet (exceeded) state surface water quality standards established to protect beneficial uses of surface waters, such as fish consumption. Fish consumption advisories have been issued for parts of the river (Spokane Regional Health District and Washington State Department of Health, 2003).

Fifteen waterbody segments of the Spokane River and Lake Spokane (also known as Long Lake, herein referred to as Lake Spokane) and one segment of the Little Spokane River are on the 2008 303(d) list for exceeding human health water quality criteria for PCBs (Table 1; www.ecy.wa.gov/programs/wq/303d/index.html).

Table 1. 303(d) Listings for Total PCBs in Spokane River Fish Tissue for 2008.

Waterbody	Reach	WB number	Watercourse Number	Listing ID
Spokane River	Idaho Border to Latah Creek	WA-57-1010	QZ45UE	Spokane River
	Latah Creek to Ninemile Dam	WA-54-1010		
Little Spokane River	Near mouth	WA-55-1010	JZ70CP	Little Spokane River
Lake Spokane (Long Lake)	Ninemile Dam to Lake Spokane Dam	WA-54-9040	QZ45UE	Lake Spokane (Long Lake)
Spokane River	Lake Spokane Dam to Mouth	WA-54-1020	QZ45UE	Spokane River

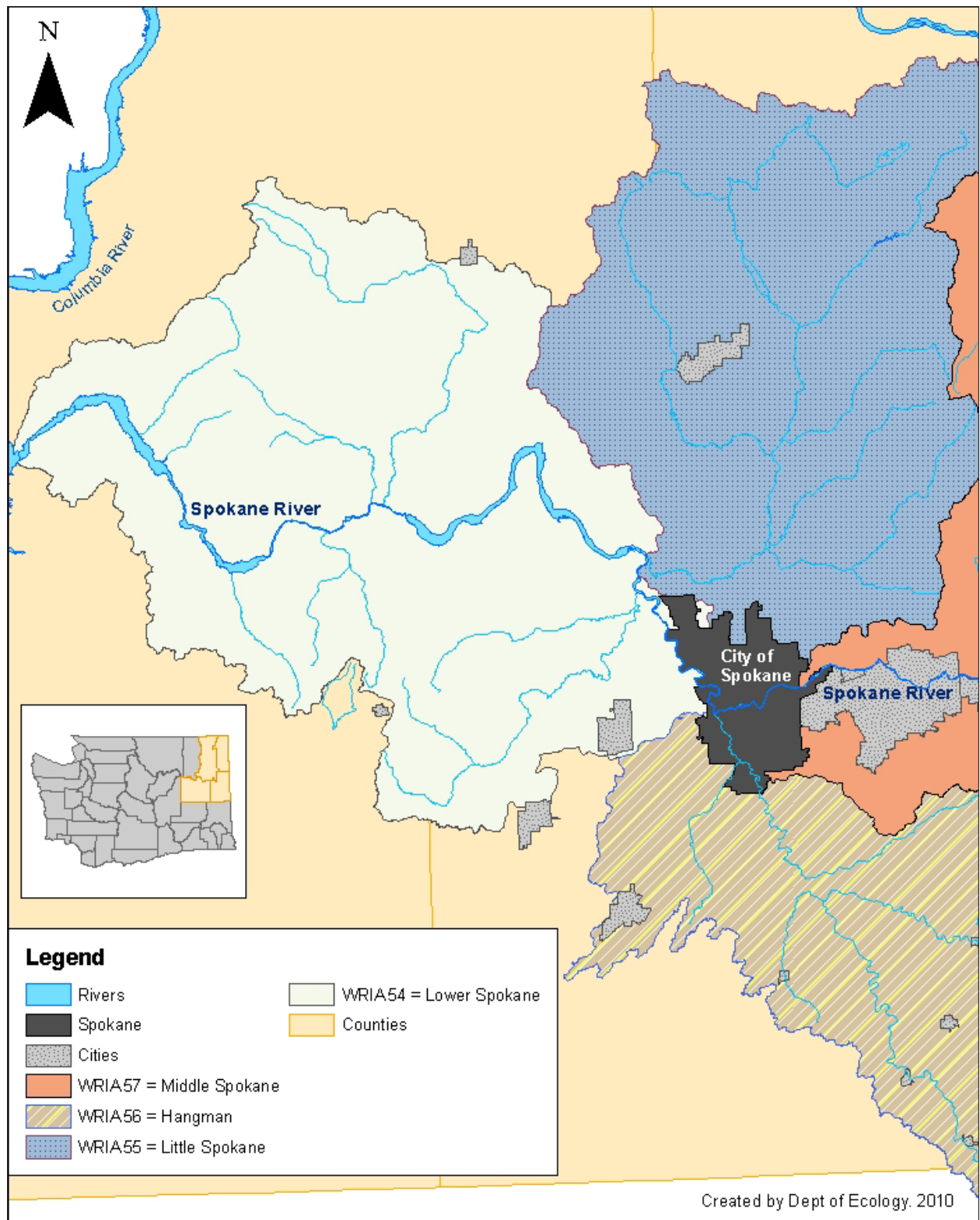


Figure 1. Location Map of Spokane River Showing Water Resource Inventory Areas.

The Spokane River and Lake Spokane have other water quality criteria exceedances that are not addressed in this source assessment. Table 2 shows the 303(d) listings for parameters other than PCBs that occur in the study area.

Table 2. Additional 303(d) Listings Not Addressed in this Report.

Waterbody	Parameter	Medium	Listing ID	Township	Range	Section
Spokane River	Temperature	Water	3737	25N	46E	06
	Total dissolved gas		15183	27N	39E	20
			15184	27N	39E	14
	Fecal coliform		16853	25N	42E	04
Lake Spokane (Long Lake)	Dioxin	Fish Tissue	42410	27N	41E	22
Spokane River			42411	26N	42E	20
			51586	26N	42E	28
			51587	25N	44E	03
Lake Spokane (Long Lake)	Dissolved oxygen	Water	40939	27N	40E	15
Spokane River			15188	26N	42E	17
			17523	25N	43E	02
			15187	25N	43E	18
			11400	25N	46E	06

The listings for dioxin in Spokane River and Lake Spokane fish are based on rainbow trout and mountain white fish collected by Ecology between 2001 and 2005 (Seiders et al., 2004, 2006, 2007). The listings are either for marginal exceedances of the human health criterion for 2,3,7,8-TCDD (dioxin) or for exceedances due to other polychlorinated dioxins and furans (PCDDs/PCDFs). These listings were not addressed in the present series of studies.

Ecology plans to address dioxin listings on a larger scale (possibly region- or state-wide) in the future. Because dioxins are often carried via air and can pollute sizeable areas not necessarily limited to watersheds, a larger TMDL footprint will likely be more effective and efficient at determining sources and subsequent evaluation of possible controls.

A TMDL for lead, cadmium, and zinc was completed for the Spokane River in 1999 (Pelletier and Merrill, 1998; Butkus and Merrill, 1999).

Water Quality Standards and Designated Uses

Applicable water quality criteria for PCBs to protect human health were promulgated by the U.S. Environmental Protection Agency (EPA) in the National Toxics Rule (NTR). The Washington State Water Quality Standards for Surface Waters (WAC 173-201A-240) contain aquatic life criteria for PCBs, and the Spokane Tribe of Indians' Surface Water Quality Standards (Resolution 2003-259) contain both human health and aquatic life-based PCB criteria. These regulations and other guidance are discussed separately below. The applicable numeric criteria are shown in Table 3.

Table 3. Water and Fish Tissue Criteria or Thresholds for Total PCBs ^a (pg/l: picograms per liter; parts per quadrillion; ng/g: nanograms per gram; parts per billion).

Regulation or Guidance	Aquatic Life - Water		Human Health ^{bc}		Fish Tissue Consumption Rate (kg/day)
	(chronic) (pg/l)	(acute) (pg/l)	Water (pg/l)	Tissue (ng/g)	
National Toxics Rule (40 CFR 131)	--	--	170	5.3	0.0065
Washington Water Quality Standards (Ch. 173-201A WAC)	$1.4 \times 10^{4(d)}$	$2 \times 10^{6(d)}$	--	--	--
Spokane Tribe Water Quality Standards (Resolution 2003-259)	$1.4 \times 10^{4(e)}$	$2 \times 10^{6(f)}$	3.37	0.1	0.0863
EPA National Recommended Water Quality Criteria (EPA, 2002)	--	--	64	2.0	0.0175
EPA Screening Value for Recreational Fishers (EPA, 2000a)	--	--	--	2.0	0.0175
EPA Screening Value for Subsistence Fishers (EPA, 2000a)	--	--	--	0.245	0.142

^a total PCBs (sum of detected Aroclors, homologue groups, or congeners).

^b based on a one-in-a-million (10^{-6}) excess lifetime cancer risk.

^c for consumption of organisms and water.

^d 24-hr average not to be exceeded.

^e A one-hour average not to be exceeded more than once every three years on average.

^f A four-day average not to be exceeded more than once every three years on average.

Regulations

National Toxics Rule

Criteria for the protection of human health were issued to the state in the NTR (40 CFR 130.36). Promulgated by EPA in 1992, and subsequently amended for PCBs in 1999, the NTR establishes numeric, chemical-specific water quality criteria for most priority pollutants. In fresh waters, human health criteria take into account the combined exposure of both drinking the water and eating fish and shellfish that live in the water. Criteria are calculated such that the upper-bound excess cancer risk is less than or equal to one in one million (10^{-6} risk level). Criteria for non-carcinogens are calculated such that effects should not be seen at exposures reflecting standard EPA exposure parameters (see equation below).

NTR human health criteria for PCBs (170 pg/l (parts per quadrillion) for a 10^{-6} risk level) were derived primarily to protect people from contaminated fish, the predominant exposure pathway. Exposure through water consumption is negligible, representing approximately 1% of the total PCB intake. The human health criteria are calculated using the following equation:

Equation 1.
$$HHC = \frac{RF \times BW \times (10^9 \text{ pg/mg})}{q1^* \times [WC + (FC \times BCF)]}$$

Where:

- HHC = human health criteria.
- RF (risk factor) = the acceptable level of cancer risk. Washington's acceptable upper-bound excess cancer risk is one in a million (10^{-6}) for a lifetime exposure.
- BW (body weight) = the average body weight of the consumer. The NTR uses an average consumer body weight of 70 kg.
- q1* (cancer slope factor) = the cancer potency of each chemical. The NTR uses a q1* of 2 per mg/kg-day for PCBs.
- WC (water consumption) = the average daily consumption of water by a consumer. The NTR uses a water consumption rate of 2 L/day.
- FC (fish consumption) = the average fish tissue consumption by a consumer. The NTR uses a fish tissue consumption rate of 0.0065 kg/day.
- BCF (bioconcentration factor) = the concentration of a chemical in tissue accumulated through gill and skin divided by the concentration in the water column. The NTR uses a BCF of 31,200 L/kg for PCBs.

The water quality criterion can be converted to an equivalent fish tissue criterion using the BCF in Equation 2, where C_w is the concentration in water and C_t is the concentration in tissue:

Equation 2.
$$BCF = \frac{C_t}{C_w}$$

NTR-equivalent fish tissue concentrations may then be calculated by $C_t = BCF \times C_w$. The calculated NTR-equivalent concentration for PCBs in edible tissue (C_t) is 5.3 ng/g (parts per billion; Table 3).

The values used by EPA to derive the NTR human health criteria are not always used by public health agencies to establish fish consumption advisories in Washington and other NTR states. The Washington State Department of Health (WDOH), which has primary responsibility for assessing the need for fish consumption advisories, examines local information about higher fish consumption rates, and sub-populations at increased risk. Additionally, differences are present in the use of chemical toxicity factors and health effect endpoints. For example, water quality criteria for PCBs are based on protection against cancer, while state fish advisories for PCBs are based on protection against non-cancer effects.

Washington State

Water quality standards for surface waters of Washington State are contained in Chapter 173-201A of the Washington Administrative Code (WAC), last amended in 2006 and approved by EPA in 2008. The numeric criteria to protect aquatic life from PCB exposure is found in WAC 173-201A-240. The acute exposure criterion for PCBs in freshwater is 2×10^6 pg/l. The chronic exposure criterion is 1.4×10^4 pg/l (Table 3).

The standards also include a provision that “Toxic substances shall not be introduced above natural background levels in waters of the state which have the potential either singularly or cumulatively to adversely affect characteristic water uses, cause acute or chronic conditions to the most sensitive biota dependent on those waters, or adversely affect public health as determined by the department (WAC 173-201A-240(1)).”

Designated uses (defined in WAC 173-201A-200(1)) in the Spokane River, from its mouth to the Idaho border include:

- Core summer habitat
- Spawning/rearing
- Recreation
- Water supply
- Harvesting
- Other miscellaneous uses

Spokane Tribe

The Spokane Tribe of Indians (Spokane Tribe) Surface Water Quality Standards (Resolution 2003-259) are similar to the Washington State Water Quality Standards in terms of narrative and numeric criteria. They apply to the westernmost part of the river defined by a line bisecting the Spokane Arm and Little Falls reservoir from river mile (RM) 32.5 to RM 0 (see Figure 2). The Tribal standards consider the Spokane River and most of its tributaries to be Class A surface water, with the exception of Blue Creek, Orazada Creek, and Sand Creek which are all Class AA tributaries to the Spokane Arm between RM 8 and RM 13. Designated uses for Spokane Tribe Class A and AA waters are similar to the Washington State standards, but also include primary contact (Washington waters are also designated for primary contact), ceremonial and spiritual, and cultural uses.

The Spokane Tribal narrative section for toxic pollutant standards is nearly identical to that of Washington State, including the adoption of a 10^{-6} risk level of for carcinogens. However, the Tribal numeric human health criteria are substantially lower (more restrictive) than those issued to Washington in the NTR (3.37 vs. 170 pg/l) due to different values used to derive the human health criteria. Tribal standards employ an aquatic organism consumption rate of 0.0863 kg/day, as opposed to the 0.0065 kg/day fish consumption rate in the NTR. In addition, the Spokane Tribe PCB criteria include an older cancer slope factor of 7.7 per mg/kg-d. Using the same approach used to derive an NTR-equivalent tissue value as described above in Eq. 2, the Spokane Tribe human health criteria of 3.37 pg/l translates to an equivalent edible tissue concentration of 0.1 ng/g.

Guidance

EPA Recommended National Water Quality Criteria

In 2002, EPA recommended new national water quality criteria including a new human health criterion for PCBs based on an upward revision of the fish consumption rate to 0.0175 kg/day (EPA, 2002). All other factors used to derive the recommended criterion (RF, BW, q1*, WC, and BCF) remained unchanged. The resulting recommended criterion for PCBs is 64 pg/l for water. The equivalent fish tissue concentration for this criterion is 2.0 ng/g (Table 3).

EPA Screening Values for Fish Advisories

Other threshold values which have no regulatory standing but are often used to assess potential public health risk are the EPA (2000a) tissue screening values (Table 3) used to evaluate fish advisories. Tissue screening values are derived in the same manner as NTR criteria and EPA's 2002 recommended national criteria, with adjustments only to the fish consumption rates. The screening value for recreational fishers is 2.0 ng/g, based on a consumption rate representing the 90th percentile of sport fishers (0.0175 kg/day). The screening value for subsistence fishers (0.24 ng/g) is based on a 99th percentile consumption rate (0.142 kg/day).

Watershed Description

Hydrology

The Spokane River begins in northern Idaho at the outlet of Coeur d'Alene Lake and flows west 112 miles to the Columbia River (Franklin D. Roosevelt Lake) (Figure 2). The watershed encompasses over 6,000 square miles (15,500 km²) in Washington and Idaho. The river flows through the smaller cities of Post Falls and Coeur d'Alene in Idaho and large urban areas of the Spokane Valley and Spokane in Washington. Other cities in the basin include Liberty Lake, Deer Park, and Medical Lake Washington as well as Wallace and Kellogg Idaho upstream from Lake Coeur d'Alene.

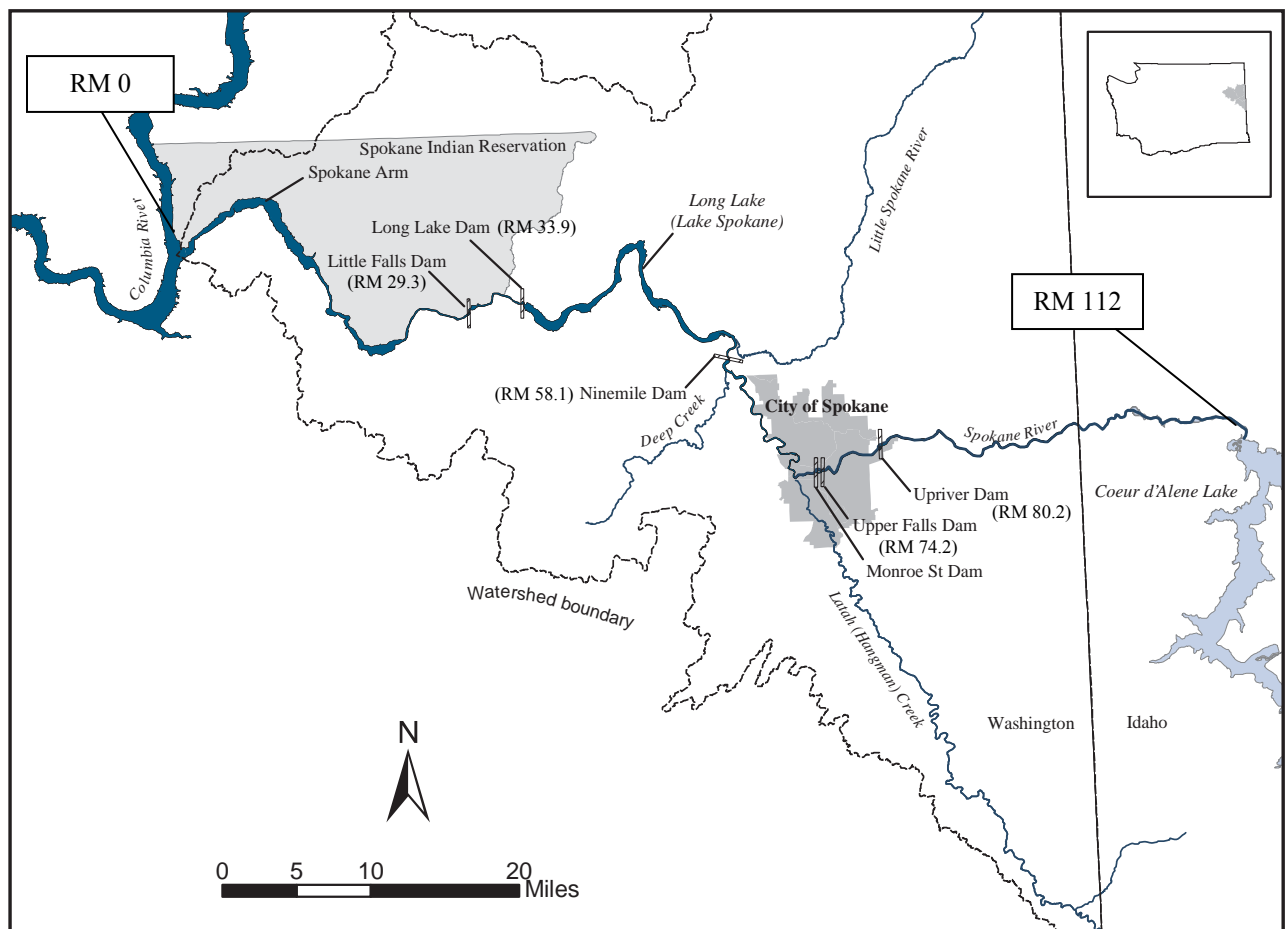


Figure 2. Spokane River Basin.

There are seven dams along the Spokane River:

1. Post Falls Dam (RM 100.8).
2. Upriver Dam (RM 80.2).
3. Upper Falls Dam (RM 74.5).
4. Monroe Street Dam (RM 74.0).
5. Ninemile Dam (RM 58.1).
6. Lake Spokane (Long Lake) Dam (RM 33.9).
7. Little Falls Dam (RM 29.3).

The dams create a series of pools which vary in length, the largest being 23-mile long Lake Spokane. Downstream from Lake Spokane, the Spokane River forms the southern boundary of the Spokane Tribe of Indians reservation from Chamokane Creek (RM 32.5) to the Columbia River at RM 639.0. The reservation occupies approximately 160,000 acres and is home to 2,441 tribal members (as of 2006).

The flow regime in the Spokane River is dictated largely by freezing temperatures in the winter followed by spring snowmelt. Figure 3 shows the harmonic mean flow at four points in the Spokane River. The harmonic mean is recommended by EPA (1991a) for use in assessing a river's loading capacity for long-term exposure to carcinogens such as PCBs. This is the appropriate measure of central tendency when dealing with rates, in this case rates of flow. Harmonic mean is discussed in more detail later in this report (see *Instream Loads*).

The annual mean flow for 1969-2002 was approximately 61,000 L/sec (2,154 cfs) where the Spokane River crosses the Idaho border. Flows increased to 82,000 L/sec (2,895 cfs) downstream of Spokane, reflecting the influx of groundwater through this river reach. Prior to 1969 there were un-quantified agricultural diversions for irrigation from the Spokane River in the vicinity of Post Falls.

Sediment

Downstream of Spokane the river corridor is largely undeveloped. The two major tributaries – Latah Creek (formerly Hangman Creek) and Little Spokane River – enter the Spokane River at RM 72.2 and RM 56.3, respectively. Latah Creek has an extremely flashy flow regime, responding rapidly to rainfall or snowmelt and is prone to erosion of its banks, thus delivering substantial sediment loads to the Spokane River (SCCD, 2002). In comparison, the Little Spokane River has an order of magnitude higher mean flow than Latah Creek, but carries slightly lower sediment loads.

One particular macro characteristic of the Spokane River is the general lack of fine depositional sediments in most of the river. Lake Coeur d'Alene acts as a settling basin for sediments transported in the upper watershed, and there are no tributaries to the river between the outlet of the lake and Latah Creek. Spokane River is essentially a free-stone stream environment. Although the dams break the river into a series of pools, there are few areas of placid water above Lake Spokane. The river velocities are high enough and the sediment load low enough to

scour the bed or prevent settling of significant fine particulate matter, even immediately behind the dams. As a result, almost the entire riverbed upstream of Lake Spokane (the largest reservoir) is composed of gravel, cobble, and boulders with the finer sediment reserved for limited locations behind the dams, interstitial spaces within the river bed, isolated shoreline deposits, and certain fluvial bar features. One notable exception is the narrow band of fine, organic carbon rich sediments found near the Upriver Dam reservoir that constituted the MTCA cleanup site, previously mentioned.

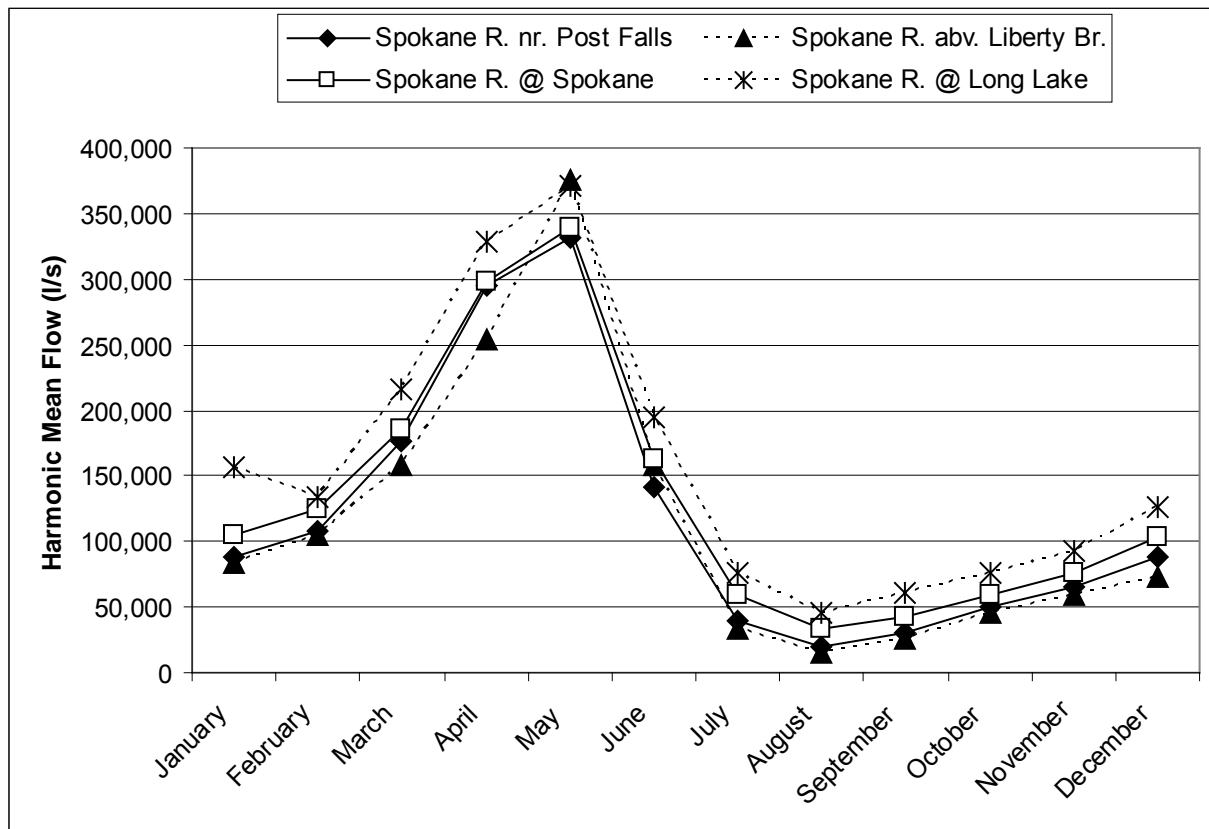


Figure 3. Spokane River Monthly Harmonic Mean Flows for Water Years 1969-2002.

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PCB Contamination of the Spokane River

Uses, Structure, and Analysis

PCBs were first produced for commercial use in 1929. Production continued until a 1979 ban on all PCB manufacturing, processing, and distribution due to evidence that PCBs build up in the environment and concerns about possible human carcinogenicity (Sittig, 1980). Principal uses were as heat transfer fluids, plasticizers, wax and pesticide extenders, lubricants, and fluids for hydraulic machinery, vacuum pumps, and compressors.

There are 209 individual forms of PCBs, known as congeners. The naming system for congeners is based on the number and location of chlorine atoms on the biphenyl rings (Figure 4).

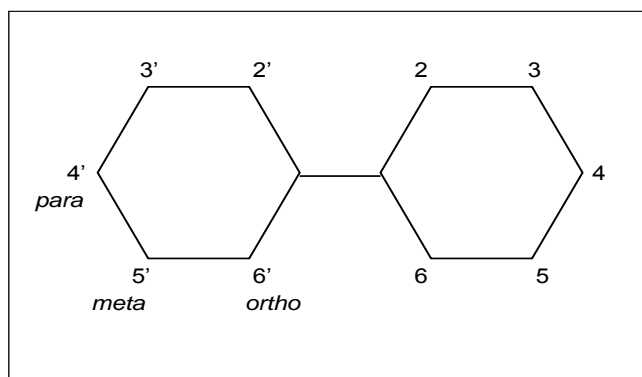


Figure 4. Generic PCB Molecular Structure and Numbering System.

In the U.S., PCBs were produced almost exclusively as Aroclors, the trade name for congener mixtures containing 21 to 68% chlorine by weight. The names given to the different Aroclors reflect this composition; Aroclor [PCB]-1248, for instance, contains approximately 48% chlorine by weight (12 refers to the number of carbon atoms in the biphenyl ring). Many different commercial Aroclor mixtures have been quantified as to their congener composition by Frame et al. (1996).

PCBs can be analyzed as individual congeners or Aroclor-equivalents. Congeners are usually analyzed by high-resolution gas chromatography/mass spectrometry (GC/MS) methods that are more costly, but more sensitive and thus give lower detection limits than the gas chromatography/electron capture (GC/ECD) method typically employed for Aroclor mixtures. Most of the historical fish tissue data for Washington State is from Aroclor analysis.

Much of the 600 million kg of PCBs used domestically has found its way into the environment through improper disposal or by leakage of sealed systems (Sittig, 1980). Loss to the environment through PCB use in open systems such as hydraulic fluids in die cast machinery, heat transfer systems, and specialty inks was also not uncommon (EPA, 2000a). Their primary uses are associated more with heavy industry or urban centers rather than agriculture (EPA,

1992). Direct application to the environment occurred on a lesser scale through use as pesticide extenders or oil mixtures applied to roads for dust control. Many of the same properties that made PCBs commercially desirable – their stability and resistance to degradation – make them extremely persistent in the environment. They have become one of the most ubiquitous of all environmental contaminants.

Environmental Fate

The persistence of PCBs increases with the degree of chlorination. Mono-, di- and tri-chlorinated biphenyls biodegrade relatively rapidly, tetrachlorinated biphenyls biodegrade slowly, and higher chlorinated biphenyls are resistant to biodegradation.

In soils, PCBs experience tight adsorption which generally increases with the degree of chlorination of the PCB. PCBs generally do not leach significantly in aqueous soil systems; the higher chlorinated congeners have a lower tendency to leach than the less chlorinated congeners. Vapor loss of PCBs from soil surfaces appears to be an important fate mechanism with the rate of volatilization decreasing with increasing chlorination.

In water, adsorption to sediment and suspended matter are important fate processes; PCB concentrations in sediment and suspended matter are typically much greater than in the water column. Although adsorption can immobilize PCBs (especially the higher chlorinated congeners) for relatively long periods of time, eventual re-solution into the water column has been shown to occur. The PCB composition in water will be enriched in the lower chlorinated PCBs because of their greater water solubility, and the least water soluble PCBs (highest chlorine content) will tend to remain adsorbed.

However, strong PCB adsorption to sediment significantly competes with volatilization, with the higher chlorinated PCBs having longer half-lives than the lower chlorinated PCBs. Lower chlorinated PCBs and ortho-substituted congeners are more volatile than the highly chlorinated PCBs. Henry's Law constants generally range from approximately 1 to 400 Pa m³/mol (Pascals cubic meter/mole), indicating volatilization is an important transport process for PCBs in the environment. PCB volatilization from water, particularly at falls or dams, and from exposed contaminated soils can be an important transport process for PCBs and, in the absence of adsorption, PCBs volatilize relatively rapidly from water.

Losses of PCBs from the Great Lakes have been estimated by Eisenreich et al. (1992) as 66% via volatilization, 27% via sedimentation, and 7% through the outflow to other waterbodies. Dam spillways may cause significant transformations of an Aroclor mixture, with differential loss of constituent congeners (McLachlan et al., 1990). The dams along the Spokane River likely modify the dissolved and particulate fractions of PCBs as water moves downstream.

The combination of differential solubility, variable octanol-water partitioning coefficients (K_{ow}), and volatilization leads to weathering of Aroclor mixtures. In environmental samples, these physical and chemical processes change the composition of released PCB mixtures over time. Thus, sediment and water samples rarely have congener patterns which match a commercial Aroclor due to weathering. If released to the atmosphere, PCBs will primarily exist in the vapor-

phase; the tendency to become associated with the particulate-phase will increase as the degree of chlorination increases. Physical removal of PCBs from the atmosphere is accomplished by wet and dry deposition.

PCBs accumulate in the lipids (fats) of fish and other animals. Lipid solubility increases with the degree of chlorination (Mabey et al., 1982), reflected in their high K_{ow} . The range of $\log K_{ow}$ is from approximately 4.6 for monochlorinated congeners to 8.2 for decachlorobiphenyl. Peak bioaccumulation occurs between $\log K_{ow}$ 6.5 and 7.0 (Fisk et al., 1998), those congeners with 5 or 6 chlorines. It is believed that congeners with $\log K_{ow} > 7.0$ are too large to be efficiently assimilated in the fish digestive tract.

All known aerobic and anaerobic biotic processes act to de-chlorinate PCBs (ATSDR, 1997). Substitution of either a hydrogen or chlorine atom is generally required by an organism to excrete a PCB molecule. Congeners which do not have chlorines in meta positions can be metabolized and excreted. Organisms preferentially metabolize and excrete different PCB congeners depending on their resistance to substitution. Substitution is generally more difficult for the richly chlorinated congeners, leading to preferential bioaccumulation of heavier, but not the heaviest, congeners.

Historical Data on PCBs in the Spokane River

Ecology has analyzed PCBs in a variety of water, sediment, and fish tissue samples collected from the Spokane River over the past two decades. Additional data have been collected by or in cooperation with the U.S. Geological Survey (USGS) and various NPDES dischargers. More recent work has focused attention on characterizing PCB contaminated sediments behind Upriver Dam. The various data collection efforts going back to 1980 are listed in Table 4.

PCBs were first analyzed in the Spokane River during Ecology statewide screening-level surveys of contaminants in fish from rivers and lakes (Hopkins et al., 1985; Hopkins, 1991; Serdar et al., 1994). Spokane River fish almost always had high PCB concentrations. For instance, total PCBs in whole fish ranged up to 2,300 ng/g (parts per billion) in northern pikeminnow (*Ptychocheilus oregonensis*) collected in 1983. Fillets from mountain whitefish (*Prosopium williamsoni*) and bridgelip sucker (*Catostomus columbianus*) from Riverside State Park in the City of Spokane were also elevated with total PCB concentrations of 230 and 370 ng/g, respectively. Largescale suckers (*Catostomus macrocheilus*) sampled from Lake Spokane had a whole body concentration of 720 ng/g.

In 1993, Ecology expanded its investigation of PCBs in the Spokane River by analyzing multiple fish species and sediments at reaches encompassing the entire river. Johnson et al. (1994) confirmed the high PCB levels seen earlier and found the highest fish tissue and sediment levels in the reach above Upriver Dam (up to 2,800 ng/g in whole largescale suckers and 3,200 ng/g in sediments) with levels gradually declining downstream.

Table 4. Summary of PCB Data Collected on the Spokane River, 1980-2007.

Investigator	Sample Type	Year Collected	Purpose
Ecology (Hopkins et al., 1985)	Fish tissue	1980-1983	Statewide survey of contaminants in rivers
Ecology (Hopkins, 1991)	Sediment	1989	Statewide survey of contaminants in rivers
Ecology (Serdar et al., 1994)	Fish tissue ^{1,2} Sediment	1992	Statewide survey of contaminants in lakes
Ecology (Johnson, et al., 1994)	Tissue Sediment	1993	Survey for PCBs in the Spokane River
Ecology (Davis et al., 1995)	Fish tissue		Statewide survey of pesticides and PCBs
Ecology (Ecology, 1995)	Fish and crayfish, tissue, sediment, surface water, effluent, sludge	1994	Synoptic survey of PCBs in the Spokane River
Hart Crowser, 1995	Effluent		Sampled Kaiser Trentwood effluent coincidental with Ecology sampling
Ecology (Huntamer, 1995)	Sediment		Microscopic examination and PCB analysis of sediments behind Upriver Dam
Ecology (Golding, 1996)	Effluent Sludge	1995	Follow-up to effluent and sludge sampling conducted during 1994 synoptic survey
Ecology (Johnson, 1997)	Fish tissue	1996	Survey to determine PCB levels in Spokane River fish
Ecology and USGS (Johnson, 2000)	Fish and crayfish tissue	1999	Survey to determine PCB levels in Spokane River fish
Ecology (Johnson and Norton, 2001)	Sediment	2000	Chemistry and bioassays of Spokane River
Ecology (Golding, 2001)	Surface water Effluent		Survey of PCBs in Kaiser Trentwood effluents and receiving waters
Ecology (Golding, 2002)	Effluent	2001	Survey of PCBs in industrial and WWTP effluents
Ecology (Jack and Roose, 2002)	Fish tissue		Intensive survey of PCBs in Lake Spokane fish
Exponent and Anchor, 2001	Sediment		Survey of PCBs in sediments behind Upriver Dam
SAIC, 2003a	Effluent Sludge	2002	Survey of PCBs in effluent and sludge from Inland Empire
SAIC, 2003b	Fish tissue		Intensive survey of PCBs in Lake Coeur d'Alene fish
Anchor Environmental (Anchor, 2004)	Surface water Groundwater	2003	Remedial investigation of PCBs in the vicinity of Upriver Dam MTCA site
Merill and Bala, 2004	Effluent	2002-2003	Bi-weekly monitoring of PCBs in Kaiser Trentwood effluent
Kaiser (Kaiser, 2005)	Effluent	2004-2005	PCBs in Kaiser Trentwood effluent
Merill and Bala, 2004	Effluent	2002-2003	Bi-weekly monitoring of PCBs in Kaiser Trentwood effluent
Ecology (Serdar and Johnson, 2006)	Fish tissue	2005	Synoptic survey of PCBs in Spokane River fish
Ecology (Seiders, Deligeannis, and Kinney, 2006)	Surface water Fish tissue		Statewide survey of toxic contaminants in waters and fish, including Spokane River
Parsons, 2007	Stormwater	2007	Survey of PCBs in Spokane stormwater

WWTP: wastewater treatment plant.

In 1994, Ecology further increased the number of organisms and locations analyzed for PCBs in the Spokane River. Results again confirmed the pattern of contamination among sites seen in 1993. The 1994 study also found that Little Spokane River fish had higher than expected PCB levels. Crayfish had low accumulations of PCBs.

The 1994 samples also included bottom sediments and potential industrial/municipal sources of PCBs to the river. This helped define the extent of contamination behind Upriver Dam, largely by delineating the area of depositional material. Nearly the entire river was surveyed for the presence of significant bulk fine sediment deposits between the state line and Lake Spokane, but the “hot spot” behind Upriver Dam was the only sediment deposit found during that study.

Perhaps the most important findings from 1994 were the characterizations of PCB sources to the river. Sewage treatment plants, industrial facilities, and industrial sites along the river were sampled to assess their relative contribution of PCBs. Results showed that sources upstream of the Idaho border were negligible, but downstream there was a substantial ongoing PCB source at the Kaiser Trentwood aluminum plant, potentially significant sources such as the Liberty Lake wastewater treatment plant (WWTP) and the former Inland Metals site, and a historically large source from the Spokane Industrial Park, which now discharged to the Spokane WWTP. Low PCB concentrations were found at a Washington Water Power yard, located just above the river bank, ruling this site out as a potentially significant source. PCB discharges from industrial and municipal treatment plants are discussed in more detail later in this section of the report.

Ecology analyzed more fish in 1996, specifically to determine if the trend toward decreasing PCB concentrations continued. The three species used most often for comparisons in the Spokane River – rainbow trout, mountain whitefish, and largescale suckers – all showed substantial decreases in PCB concentrations from earlier data (Table 5). However, PCB levels continued to remain high relative to other areas in the state.

Since 1999, surveys in the Spokane River have verified previous data or further characterized the contamination so that its implications are better understood. The three major areas where study efforts have concentrated in the past decade are:

- Continued sampling of fish to evaluate temporal trends and conduct human health risk assessment.
- Continued monitoring of known PCB sources.
- Characterization of the Upriver Dam cleanup site.

In July 1999, USGS collaborated with Ecology to further document PCB contamination in fish from the mainstem of the Spokane River (USGS, 1999; Johnson, 2000). This study found that whole largescale suckers exceeded a criterion of 110 ng/g used to protect fish-eating wildlife (Newell et al., 1987). Concentrations in whole suckers ranged from 120 to 700 ng/g total PCBs. For mountain whitefish and rainbow trout (*Oncorhynchus mykiss*), fillets and whole fish were analyzed. Peak concentrations were found in rainbow trout in the vicinity of RM 85 (Plante Ferry) and in mountain whitefish in the vicinity of RM 63 (Ninemile). Maximum concentrations were about 1,600 ng/g for both species.

Table 5. Summary of Total PCB Concentrations in Fish Tissue from the Spokane River (mean concentrations in ng/g, ww).

Location and Tissue Type	Total PCB Concentrations Measured by:					
	Aroclor Analysis					Congener Analysis
	1993 ^a	1994 ^b	1996 ^c	1999 ^d	2001 ^e	2005 ^f
Rainbow trout - fillet						
State line	--	--	--	106	--	55
Plante Ferry	918	424	799	891	--	153
Above Monroe Dam*	--	145	76	226	--	73
Ninemile	490	371	76	143	--	
Mountain whitefish - fillet						
Above Monroe Dam	--	568	381	339	--	234
Ninemile	522	139	444	632	--	139
Little Spokane	--	222	145	--	--	--
Upper Lake Spokane	--		--	--	73	43
Lower Lake Spokane	780	113	--	--	--	76
Largescale suckers - whole						
State line	--	--	--	120	--	56
Plante Ferry	2,005	531	530	283	--	122
Above Monroe Dam	--	201	116	445	--	1,823
Ninemile	1,210		345	680	--	--
Little Spokane	--	440	366	--	--	--
Upper Lake Spokane	--	--	--	--	265	327
Lower Lake Spokane	410	820	--	--	357	254

--no data

^a Johnson et al., 1994^b Ecology, 1995^c Johnson, 1997^d Johnson, 2000^e Jack and Roose, 2002^f Serdar and Johnson, 2006

*Same reach as Mission Park

In 2001, Ecology, WDOH, and the Washington Department of Fish and Wildlife (WDFW) collaborated in the collection of five species to evaluate PCB concentrations in Lake Spokane fish tissues (Jack and Roose, 2002). In general, largescale suckers and mountain whitefish had the highest PCB concentrations. Total PCBs in whole suckers ranged from 160 to 340 ng/g, while mountain whitefish fillets ranged from 60 to 89 ng/g. The greater uptake and retention of PCBs in suckers is likely influenced by their relatively high lipid content, benthic (bottom feeding) habits, limited capabilities for PCB excretion, and longevity. Largescale suckers analyzed from Lake Spokane were up to 24 years old (Jack and Roose, 2002). Fish consumption advisories were issued in 2003 and are further discussed below.

In 2005, another intensive study was conducted to expand and update the information on chemical contaminants in Spokane River fish (Serdar and Johnson, 2006). Fish from six locations between the Washington/Idaho state line and lower Lake Spokane were collected. Samples of fillets and whole fish were analyzed for PCBs, polybrominated diphenyl ether flame

retardants (PBDEs), arsenic, cadmium, lead, and zinc. A subset of samples was also analyzed for polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDFs).

Compared to historical levels, PCB concentrations appeared to have decreased in all parts of the Spokane River except the Mission Park reach. Relative to other parts of the state, Spokane River fish were within the mean and median for fillet PCB concentrations. However, whole fish results for Mission Park and Lake Spokane were at or above the upper end of the range of whole fish statewide.

Spokane River fish also substantially exceeded statewide comparisons for concentrations of PBDEs, zinc, lead, and cadmium (whole fish samples only). The Urban Waters Program at Ecology is currently pursuing sources of PBDEs to the river. Metals contamination of the Spokane River is from historic mining in Idaho's Silver Valley and has been the subject of many past studies. As previously mentioned, a TMDL has been established for lead, cadmium, and zinc in the Spokane River.

Ecology's Washington State Toxics Monitoring Program also sampled fish from the Spokane River in 2003-04 for a suite of toxic compounds. PCBs were not analyzed due to concurrent intensive PCBs surveys on the river. A recommendation from this effort was to list the Spokane River as impaired on the 303(d) list for 2,3,7,8-TCDD (dioxin) (Seiders et al., 2006).

Table 5 provides a comparison of the total PCB concentrations from the various Ecology studies.

Fish Consumption Advisories

Based on the elevated PCB and lead levels in Spokane River fish, WDOH and the Spokane Regional Health District issued an advisory in 2003 to avoid or limit consumption of fish in parts of the Spokane River

(www.doh.wa.gov/ehp/oehas/fish/consumpadvice.htm#Spokane%20River). The health departments later concluded that the advisory would also be protective for PBDEs. The advisory, updated in April 2008 based on fish tissue samples collected for the present 2003-07 study, is summarized in Table 6.

Table 6. April 2008 Spokane River Fish Consumption Advisories.

Location	Species	Consumption Advice
Spokane River – All Areas	All Species	Do not eat the fish head or entrails.
Idaho Border to Upriver Dam	All Species	Do not eat
Upriver Dam to Ninemile Dam	Largescale Sucker	Do not eat
	All Other Species	One meal per month
Lake Spokane (Long Lake)	Largescale Sucker	One meal per month
	Brown Trout	
	Largemouth Bass	Two meals per month
	Smallmouth Bass	
	Rainbow Trout	Two meals per week
	Yellow Perch	

National Pollutant Discharge Elimination System (NPDES) Permits

Ecology has issued NPDES wastewater discharge permits to a variety of industrial and municipal facilities in the Spokane River basin. Some of these facilities have discharged PCBs in the past. Ecology-directed MTCA sediment cleanup actions upstream of Upriver Dam identified the Kaiser Trentwood facility and the Spokane Industrial Park as the most prominent historic sources of PCB releases in that portion of the river. Recent studies have confirmed the presence of PCBs in the waste streams of some permitted Spokane River dischargers. Appendix A lists the permitted discharges to the greater Spokane watershed by WRIA and permit number.

The NPDES permits in Appendix A are coded based on the type of discharge to waters of the state. Those permit numbers beginning with ST are for the discharge of municipal and industrial effluents to ground or industrial effluents to municipal sewer systems. The City of Spokane WWTP receives effluent from a number of these industrial dischargers. Permit numbers beginning with WAG are general NPDES permits. “WA” permits are those allowing discharge of effluents to surface waters.

In addition to the industrial and municipal discharges in Appendix A, the City of Spokane has a partially combined sewer-stormwater system. Spokane is permitted for stormwater discharges under the NPDES Phase II program. A combined sewer is a conjoined system of (1) stormwater collection from areas such as roofs and parking lots and (2) raw sewage. During heavy rain or snowmelt events, the influx of stormwater to the combined system may overwhelm its carrying capacity. At that time, a combined sewer overflow (CSO) event occurs, and a portion of the stormwater-sewage mixture bypasses the local WWTP and discharges directly to the river.

There are a total of 24 CSO points within the City of Spokane (City of Spokane, 2002). These sewers may discharge during high-flow periods or inadvertently during maintenance activities. Because of the variety of previous uses of PCBs, they may be discharged to the river during these overflow events. Some of the stormwater is delivered directly to the river through storm sewers and into ground via drywells or infiltration basins.

Historic NPDES Effluent PCB Concentrations

Some of the NPDES-permitted effluents discharged to the Spokane River have been sampled for PCBs by Ecology and others (Table 7). Ecology (1995), Golding (1996, 2001, 2002), and SAIC (2003a) report effluent data from July 1994 through June 2002 (Table 7). These samples were analyzed by both Aroclor-equivalents and congener-specific methods. While the methods may not be directly comparable to each other, these data are included to illustrate the range of loads and potential variability from these sources.

Historic PCB loads from the Kaiser Trentwood aluminum mill were consistently higher than other facilities by about an order of magnitude, although loads appear to have declined from 1994 to 2001. Kaiser also monitored PCBs in their outfall bi-weekly in 2002 and 2003 (Merrill and Bala, 2004). The median concentration of total PCBs in 2002 was 2,700 pg/l (140 mg/day), decreasing to 1,200 pg/l (90 mg/day) in 2003.

PCB concentrations in Kaiser effluent during 2002-2003 were generally consistent, with variability expressed by peaks – an order of magnitude increase from normal levels – occurring at two to five month intervals. The monitoring result for 4/9/2002 showed an unusually high PCB level in the effluent, 2.2×10^6 pg/l (0.125 kg/day), which persisted for a maximum of three weeks before returning to typical levels. PCB levels jumped again in November 2002 when four consecutive monitoring events from 11/18/2002 to 12/29/2002 found effluent concentrations of 2.6×10^7 pg/l, 3.2×10^6 pg/l, 4.8×10^7 pg/l, and 3.4×10^6 pg/l. Assuming an average daily load of 0.99 kg/day for a period of six weeks (one week prior to discovery until one week following the last elevated measurement), approximately 53 kg total PCB was delivered to the Spokane River from the Kaiser facility during this period.

Table 7. Summary of Spokane Area PCB Point Source Data.

Source	Date	Method	Total PCBs (pg/l)	Identified Aroclor	Effluent Flow (ML/day)	PCB Load to River (mg/Day)
Kaiser Trentwood	08/1/94 ^a	Aroclor	21,000	PCB-1248	109	2,290
	12/5/95 ^b		29,000		67.8	1,970
			34,000			2,300
	12/6/95 ^b		25,000		68.5	1,710
			29,000			1,990
	08/14/00 ^c		53,000	96.1	5,100	
	08/15/00 ^c		900 U	96.1	0	
			900 U		0	
			25,000	PCB-1248	2,400	
	05/1/01 ^d		10,174 NJ	NA	62.1	630
05/2/01 ^d	5,165 NJ	320				
Spokane WWTP	05/1/01 ^d	congener	1,813 NJ	NA	142	260
	05/2/01 ^d		1,767 NJ			250
Liberty Lake WWTP	05/1/01 ^d	congener	1,917 NJ	NA	2.46	4.7
	05/2/01 ^d		1,543 NJ			3.8
Inland Empire Paper	05/1/01 ^d	congener	2,436 NJ	NA	16.3	40
	06/5/02–a.m. ^e		5,484		20.0	110
	06/5/02–p.m. ^e		4,305		18.0	78
Spokane Industrial Park	07/31/94 ^a	Aroclor	9,000 U	NA	*	*
	08/4/94 ^a		31,000 U			
	05/1/01 ^d	congener	9,371 NJ			
	05/2/01 ^d		7,108 NJ			

Bold: Analyte detected

NJ: There is evidence that the analyte is present. Associated numerical result is an estimate.

U: Analyte not detected at or above the reported value.

NA: not applicable

ML/day: 0.264 MGD (million gallons per day)

* Currently discharges to Spokane WWTP; formerly discharged to Spokane River.

^a Ecology, 1995

^b Golding, 1996

^c Golding, 2001

^d Golding, 2002

^e SAIC, 2003a

PCB levels in effluent samples collected from the Spokane WWTP, Liberty Lake WWTP, and Inland Empire Paper in 2001-2002 ranged from 1,543 to 5,484 pg/l. Higher concentrations of 7,108 and 9,371 pg/l were reported in effluent from the Spokane Industrial Park analyzed in 1994. This facility now discharges to the Spokane WWTP.

PCBs Behind Upriver Dam, 1995-2004

As mentioned previously, bulk fine sediment deposits are sparse in the Spokane River upstream of Lake Spokane, with the exception of scattered shoreline, bar feature, and lower energy zones. Two notable exceptions are the narrow bands of silt and organically-enriched sediments deposited behind Upriver Dam (Figure 5).

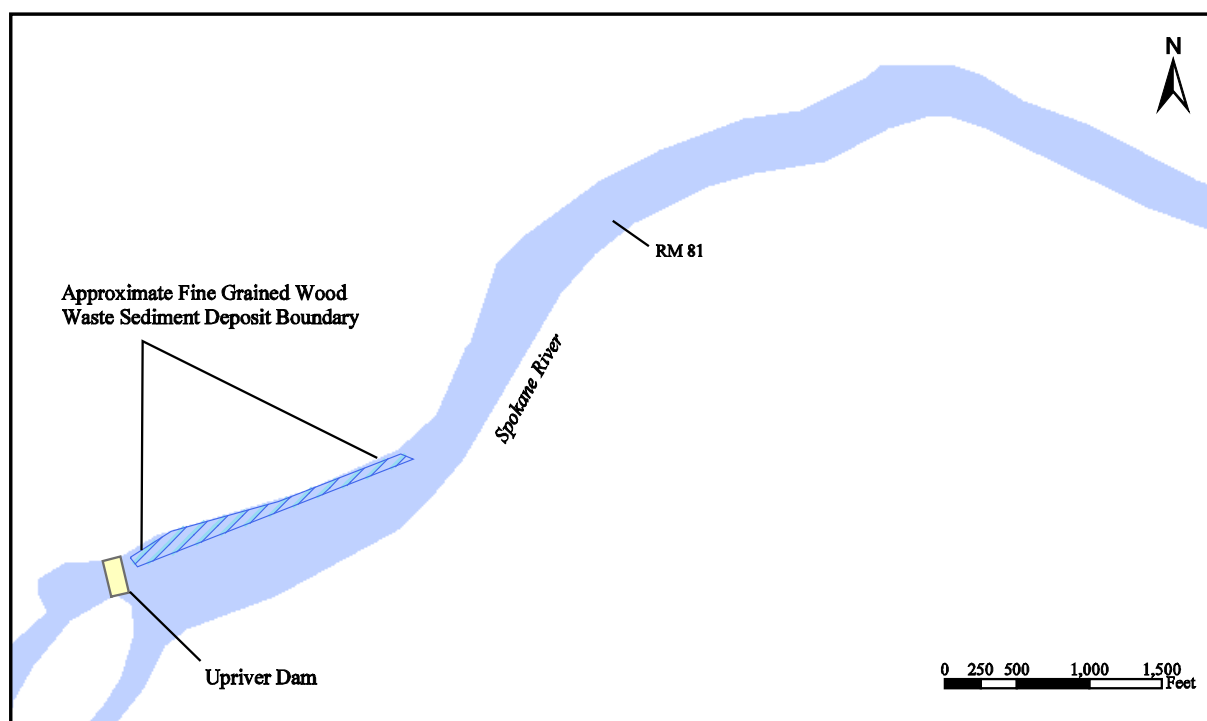


Figure 5. Location of Fine-Grained Wood Waste Sediment Deposit Behind Upriver Dam.

Following discovery of PCB contamination behind Upriver Dam in 1993 and confirmation of high PCB levels in 1994, subsequent sampling consisted mainly of defining the boundary of contamination and distribution of fine sediments upstream of the dam. Sediments within a band located immediately behind the dam generally showed PCBs at 1,000-5,000 ng/g dry weight (dw) and in some samples contained >10% total organic carbon, gradually becoming sandier at the margins (Ecology, 1995; Johnson and Norton, 2001). Huntamer (1995) conducted a microscopic analysis of the organic-enriched sediments and found them to be largely composed of wood particles, consistent with un-aided visual observation made earlier. Huntamer also observed charcoal which he speculated may have originated from recent wildfires in the area.

In February 2003, Ecology entered into a Consent Decree with Kaiser and Avista (formerly Washington Water Power) to evaluate site conditions at Upriver Dam. The remedial investigation (RI) and feasibility study (FS) (Anchor 2005a and 2005b) required under the Consent Decree informed decisions that led to the completion of a cleanup under MTCA. Aside from sediment characterization, the RI/FS addressed other components of the aquatic ecosystem associated with the Upriver Dam contamination, such as sampling PCBs in the water column and in hydraulically-connected groundwater wells, as well as bathymetric surveys of the reach.

Groundwater monitoring in the area indicates there is localized loss of surface water to the aquifer due to the hydraulic difference between the reservoir pool and the river surface downstream of the dam. Monitoring wells located downgradient of the dam showed low PCB concentrations (9-116 pg/l), which were in the range of associated field and laboratory blanks (10-226 pg/l), suggesting the presence of PCBs was due to sampling or lab contamination rather than PCB movement from the reservoir to groundwater (Anchor, 2004).

Surface water sampling was conducted both upstream and downstream of the Upriver Dam site as part of the RI/FS. During the RI/FS, upstream surface water samples and surface water samples collected at the Upriver Dam site (120 and 110 pg/l respectively) exceeded the EPA National Recommended Water Quality Criterion of 64 pg/l. As being an applicable, relevant, and appropriate requirement (ARAR) under MTCA, the 64 pg/l criterion was selected as the surface water criterion at the Upriver Dam site.

Numerous sediment samples were analyzed in and around the known area of contamination as part of the RI/FS. Samples were also collected upstream in backwaters identified as potential depositional areas. Results identified a second significant fine sediment deposit above Upriver Dam at RM 83.4 (Donkey Island) and corroborated earlier findings that deposited fine material and elevated PCB concentrations are absent outside the known areas of bulk fine sediment accumulation.

The Cleanup Action Plan by Ecology (2005) identified a sediment cleanup value of 62 µg/kg total PCBs as protective of human health and the river ecological community. The 62 µg/kg PCB sediment cleanup value was derived for the protection of aquatic life inhabiting the upper layer (0 - 10 cm) of the sediment. The selected sediment cleanup level is based on the lowest apparent effects threshold (AET) suggested for use in freshwater sediments (Michelson, 2003).

The Upriver Dam cleanup was completed in January 2007. A sediment cap was placed over the primary contaminated area on the river bed behind Upriver Dam (Deposit 1) using an excavator on a floating barge. A second smaller area of contaminated sediment was excavated in the Donkey Island area just east of Argonne Road (Deposit 2). The sediment cap that was placed at Deposit 1 was required to be 13 inches in depth. Of the 13 inches, 4 inches were bituminous coal, followed by 6 inches of clean sand, and then armored with 3 inches of gravel. The total size of the cap at Deposit 1 encompassed approximately 3.5 acres. Deposit 2 covered approximately 0.2 acres of contaminated sediment that was excavated as part of the remedial action. The estimated amount of contaminated sediment that was excavated at Deposit 2 is 600 cubic yards.

The first scheduled monitoring event at Deposit 1 to check the integrity of the sediment cap and sample the sediments for PCBs began in the fall of 2008. The results of the 2008 monitoring event found that the cap was fully intact with an additional 1 to 2 feet of deposited sand and woody material on top of the cap. The additional material is suspected to be as a result of the high spring-runoff flows that occurred in 2008. The core samples that were taken of the cap and the grab samples of the newly deposited sand did not detect PCBs higher than the cleanup value.

2003-2007 PCB Source Assessment

Goals

Sampling for the Spokane River PCB source assessment study was initially conducted by the Ecology Environmental Assessment Program from September 2003-July 2004. Additional fish and stormwater samples were collected in late 2005 and early 2007, respectively. The overall goal of this effort was to quantify PCB contamination and identify necessary reductions in sources and the receiving waters to meet applicable PCB water quality criteria for the Spokane River.

Objectives

Specific objectives of the study were to:

1. Obtain representative data on PCB concentrations and ancillary parameters in the Spokane River water column, NPDES permitted discharges, bottom sediments, and fish tissue.
2. Assess trends and natural recovery rates for PCBs in Spokane River sediments.
3. Determine the Spokane River's loading capacity for PCBs.
4. Evaluate a food web bioaccumulation model to predict PCB concentrations in Spokane River fish.

The first objective was addressed by sampling PCBs in industrial and municipal effluent, surface water, suspended particulate matter, stormwater, surface and sub-surface sediments, and fish tissue.

The second objective was achieved by analyzing PCBs in sediment cores.

Water column PCB measurements from semi-permeable membrane devices, a passive sampling technique, were used to assess the loading capacity of the Spokane River. Estimates of the PCB load reductions needed to meet the more stringent human health criteria of the Spokane Tribe were based on loading capacity and on current estimates of PCB discharges in effluent and stormwater.

The Arnot-Gobas food web bioaccumulation model (Arnot and Gobas, 2004) was employed to estimate site-specific critical PCB concentrations in water and sediment. Needed load reductions to meet water quality criteria were then estimated using PCB loading capacities derived from the model.

Field Data Collection

Sampling Locations

Sampling station locations for the source assessment study are shown in Figures 6-10. Coordinates and a description of each station location are in Appendix B.

For the purpose of this report, “Stations” are identical to the “User Location ID” in Ecology’s Environmental Information Management (EIM) database (available on the internet at www.ecy.wa.gov/eim/). All of the data for this project are available through EIM under the User Study ID named “DSER0010”, with two exceptions:

- 1) The Ninemile rainbow trout fillet data are under the User Location ID “Spokane-F” or the User Study ID “WSTMP03T”.
- 2) The 2007 stormwater data from the Parsons, (2007) study were entered into EIM under the User Study ID “brwa0004”.

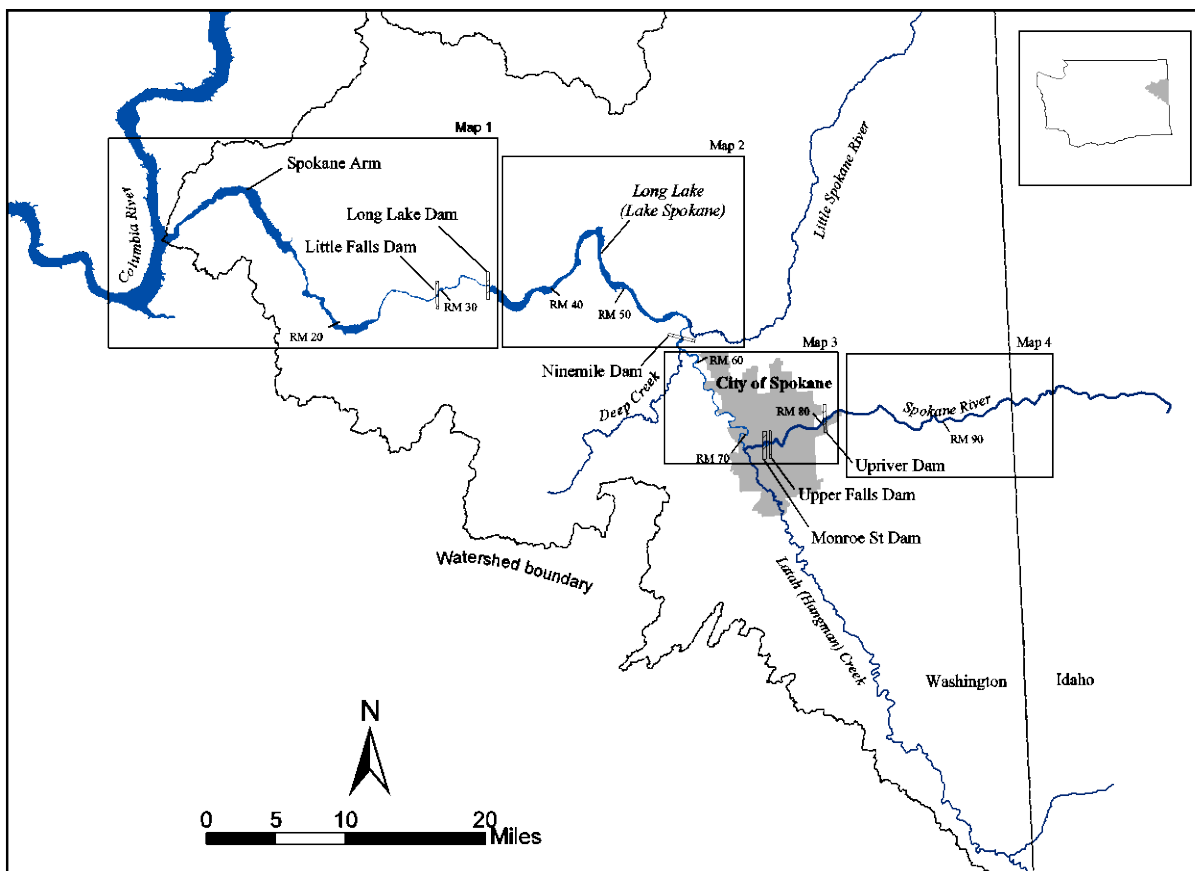


Figure 6. Sampling Maps for Spokane River PCB Source Assessment Study.

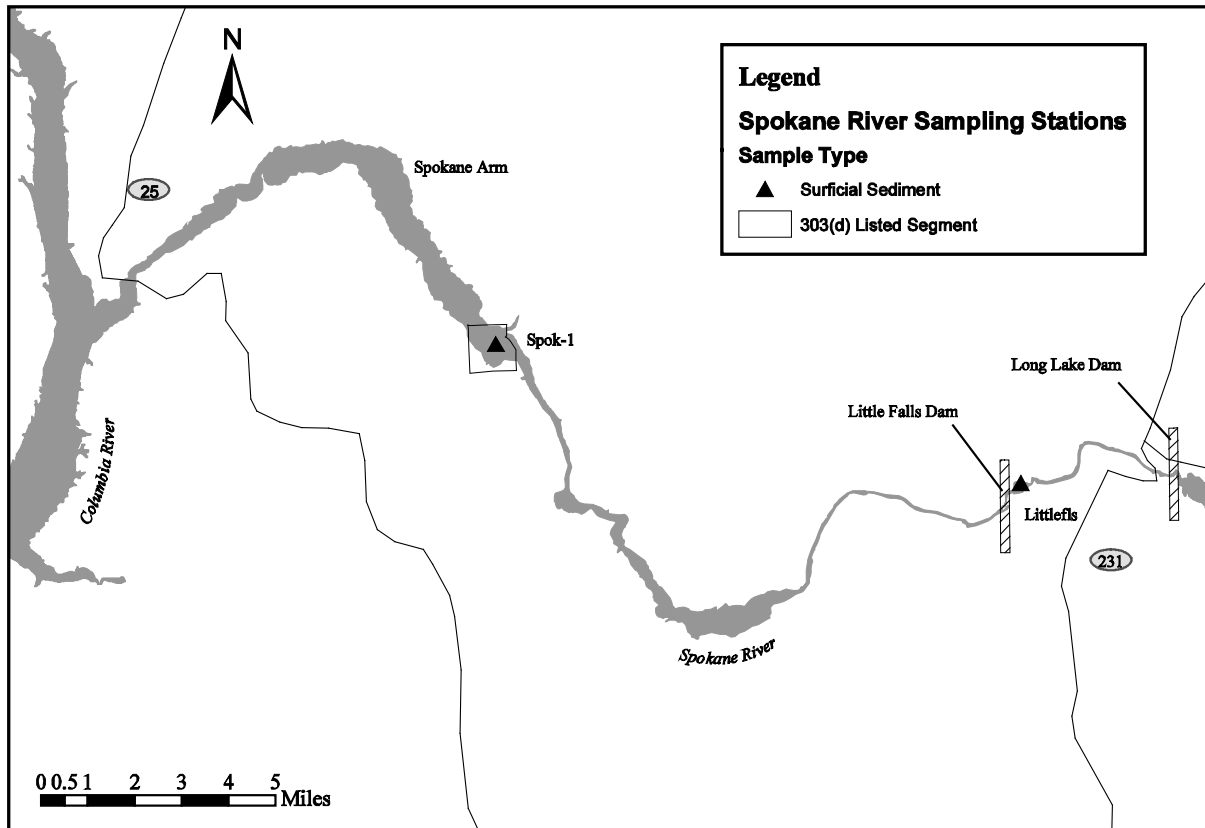


Figure 7. Sampling Map 1: Spokane River Mouth to Long Lake (Lake Spokane) Dam.

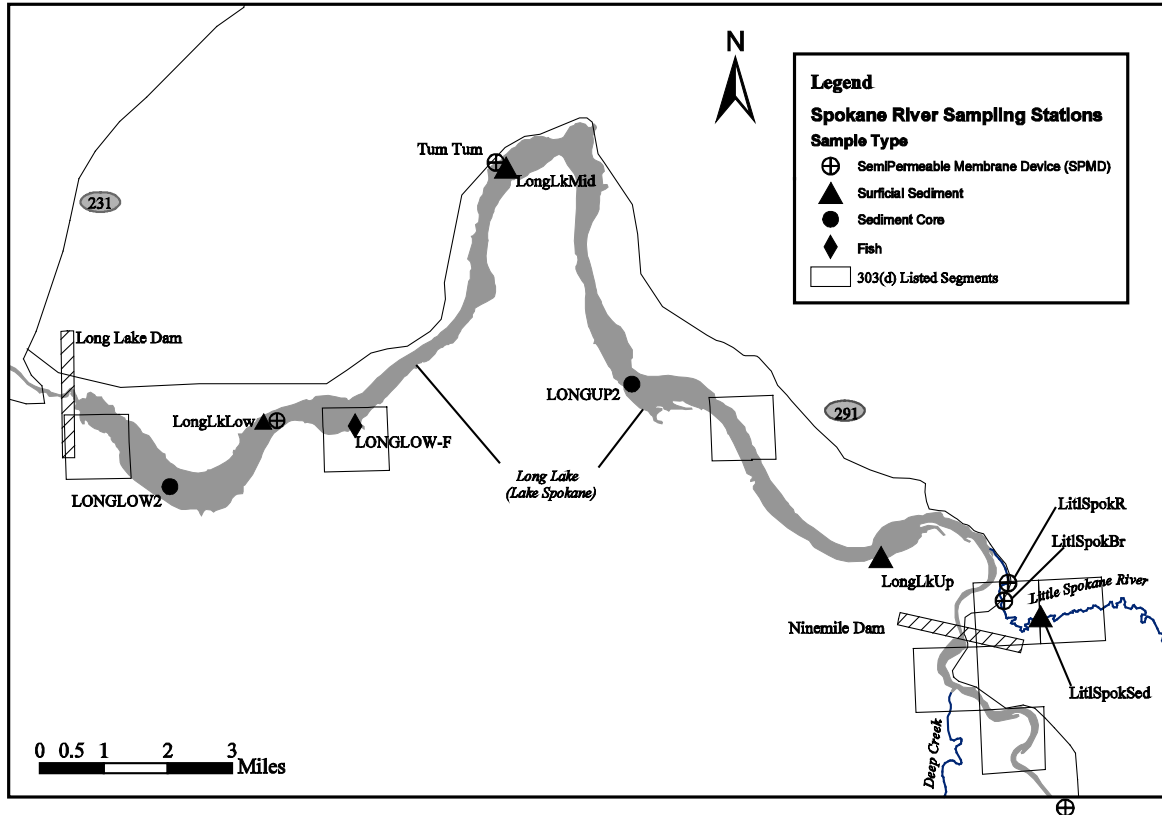


Figure 8. Sampling Map 2: Long Lake (Lake Spokane) Dam to Ninemile Dam.

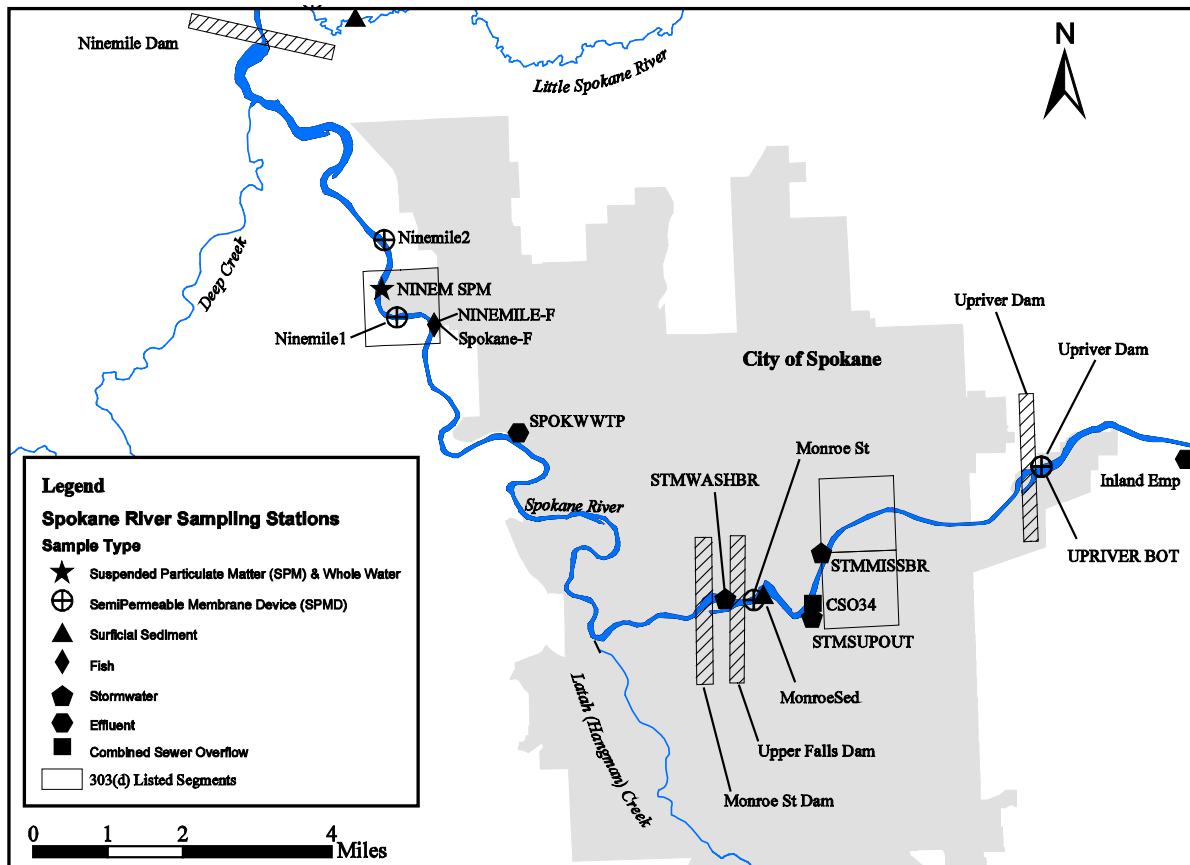


Figure 9. Sampling Map 3: Ninemile Dam to Upriver Dam.

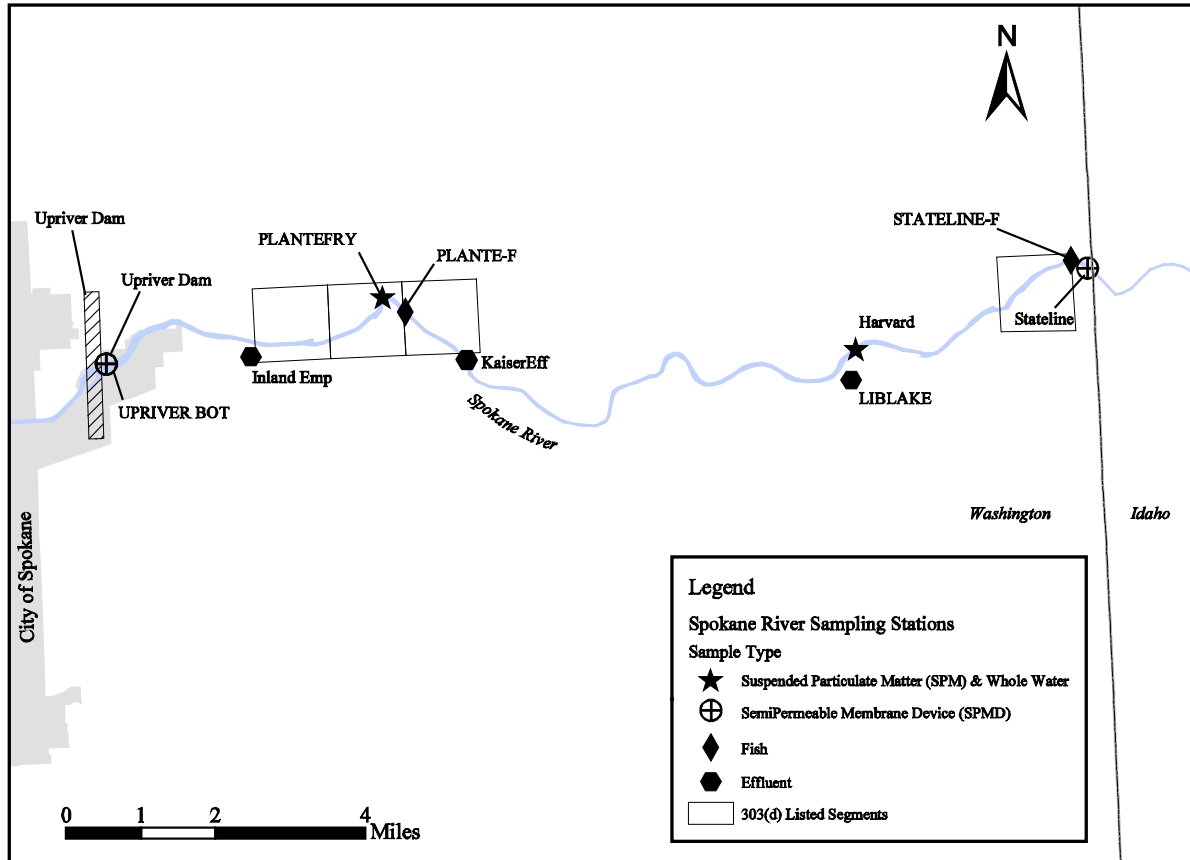


Figure 10. Sampling Map 4: Upriver Dam to Idaho Border.

Surface Water

Semipermeable Membrane Devices

Surface water at five Spokane River and one Little Spokane River locations was sampled using semipermeable membrane devices (SPMDs) obtained from Environmental Sampling Technologies (EST). SPMDs are passive samplers which consist of a 91 x 2.5 cm lay-flat polyethylene membranes filled with 1 mL triolein, a synthetic lipid that mimics biological uptake of dissolved organic compounds like PCBs. Membranes are mounted on “spider carriers” that hold the membranes during deployment and placed inside perforated stainless steel canisters, up to five membranes per can. The chemical residues accumulated in an SPMD can be used to calculate the ambient water column concentration for the chemicals of interest. Detailed information on SPMDs is in Appendix C. Table 8 shows locations where SPMDs were deployed.

Table 8. Locations and Dates of SPMD Deployments.

Location	Station	RM	Dates
State line	Stateline	96.1	10/1 - 10/29/2003 1/28 - 2/24/2004 4/14/04 - 5/12/2004
Behind Upriver Dam at mid-depth	Upriver Dam	80.3	10/1 - 10/29/2003 1/28 - 2/25/2004 4/14 - 5/12/2004
Behind Upriver Dam near bottom	UPRIVER BOT	80.3	10/1 - 10/29/2003 1/28 - 2/25/2004 4/14 - 5/12/2004
Behind Monroe St./Upper Falls Dam	Monroe St	74.8	10/2 - 10/29/2003 1/28 - 2/25/2004 4/14 - 5/12/2004
Ninemile Dam Pool upstream of Plese Flats	Ninemile1	63.6	10/1 - 10/29/2003 1/28 - 2/24/2004*
Ninemile Dam Pool near Sevenmile Bridge	Ninemile2	62.4	4/14 - 5/12/2004
Tum Tum	Tum Tum	44.2	1/29 - 2/24/2004
Lower Lake Spokane	LongLkLow	38.4	10/2 - 11/4/2003 4/13 - 5/11/2004
Little Spokane River at Rt. 291 bridge	LitlSpokBr	1.1	1/29 - 2/24/2004 4/14 - 5/12/2004
Little Spokane River ½ mile upstream of mouth	LitlSpokR	0.5	10/2 - 10/30/2003

*SPMD lost.

Canisters were deployed in the middle of the water column at Stateline, behind Upriver Dam, behind Upper Falls Dam (Monroe St.), upstream of Seven Mile Bridge (Ninemile), in Lake Spokane, and in the Little Spokane River near the mouth. In addition to the mid-depth SPMDs, deployments were also done approximately one foot above the bottom at the Upriver Dam site. The project plan called for one additional SPMD deployment in the lower two miles of Deep Creek, but the creek was too shallow for the sampler (Jack et al., 2003).

SPMD deployments occurred during October 2003, January-February 2004, and April-May 2004. These periods were selected to represent a range of river conditions: low flow in October, moderate flow in February, and high flows during spring runoff. Exposure periods were generally 28 days.

On arriving at the sampling site, the cans were opened, spider carriers were slid into the canisters, and the device was suspended in the water column. Because SPMDs are potent air samplers, the procedure was done as quickly as possible, typically one minute or less. Air exposure times were recorded for each event. Three SPMD membranes were used in each canister, with two canisters per sampling site. The dual canisters were used to minimize the risks of loss or vandalism. If both canisters were successfully recovered, the six membranes were combined for extraction. During each deployment period, one of the SPMD pairs from Upriver Dam was analyzed separately as a replicate. The dual canisters were deployed several meters apart at each station.

In some cases, alternative site selection was necessary due to variable flows or ice. The Lake Spokane SPMD was moved upstream to Tum Tum in January-February because the lower lake was frozen. The April deployment at Ninemile was moved downstream due to high flows, and the Little Spokane site was moved upstream from its original location for February and April sampling to improve accessibility. One of the two canisters was lost at Ninemile during October and at Stateline in April-May. In both instances the single canister (with three membranes each) contained enough material for complete analysis without compromising data quality. Both canisters were lost from Ninemile during January-February, the only event with lost data.

The SPMD retrieval procedure was essentially the opposite of deployment. Cans holding the SPMDs were sealed and shipped back to EST for extraction. EST then shipped the extracts to an accredited contract laboratory, Pace Analytical Services Inc., for PCB analysis.

A trip/field blank was prepared for each SPMD deployment by exposing dedicated membranes to air for the average time sample membranes were exposed. Trip blank membranes were treated the same as other membranes before and after sampling.

Temperature was monitored at 30-minute intervals throughout each deployment using a Tidbit® or I-button® temperature logger attached to the SPMD canister. At the beginning and end of each deployment period, grab samples for total organic carbon (TOC), dissolved organic carbon (DOC), and total suspended solids (TSS) were collected.

Suspended Particulate Matter and Whole River Water

Suspended particulate matter and whole water samples were collected at several locations to further assess water column PCB concentrations. Since hydrophobic organic chemicals like PCBs preferentially sorb to suspended particles, concentrations are more readily detectable, making it a useful surrogate for whole water. Suspended particles were collected using Sedisamp II continuous-flow centrifuges (model 101IL) in a manner described by Serdar et al. (1997) and previously used to collect particles in the Spokane River (Ecology, 1995). Table 9 shows locations and dates for sampling.

Table 9. Locations and Sampling Dates for Suspended Particulate Matter and Whole River Water.

Location	Station	RM	Dates (2003)
Harvard Road	Harvard	92.8	10/20 – 10/22
Plante Ferry Park	PLANTEFRY	84.8	10/28 – 10/30
Ninemile Pool at Plesse Flats	NINEM SPM	63.2	11/3 – 11/5

A peristaltic pump set at a rate of 3-4 L/min. was used to draw water from an intake strainer situated in the middle of the water column approximately 10-20 meters offshore. All tubing and fittings were Teflon®, except for Silastic® tubing used at the pump head, and all centrifuge bowl parts in contact with samples were high quality stainless steel.

Water samples for TSS were collected from the centrifuge intake and outlet water each day to estimate particle removal efficiency. TOC and DOC samples were also collected during suspended particle sampling. Aliquots of intake water were periodically collected to provide a composite sample of whole river water for PCB analysis. Once sufficient material was obtained, the centrifuges were disassembled. Then the particulate matter was removed using a Teflon® spatula, and the particulate matter placed in appropriate sample containers. All samples were stored on ice in locked coolers while in the field.

Total mass of particulate matter collected was 9-17 g (dry weight), extracted from 8,700-9,600 L of river water. TSS concentrations in whole river water averaged 1-2 mg/L, and no TSS was detectable in the centrifuge outlet water at a reporting limit of 1 mg/L. Based on the average TSS values in the river and the dry weight of the particulate matter collected, the centrifuge extraction efficiencies were 71-89%, which is in the range of typical values using these centrifuges in similar water conditions (Yake, 1993). Ancillary data for suspended particulate samples are in Appendix D.

Effluents

Industrial and Municipal Wastewater Effluent

Final effluent from wastewater streams of four facilities were collected during unannounced visits on three occasions (Table 10). Samples were composites from two consecutive days,

except at Kaiser Trentwood where final effluent was collected as discrete samples each day. Composite grab samples were also collected at the Kaiser wastewater stabilization lagoon and at the outlet of bed filters to assess the effect of particle removal on PCB concentrations.

Table 10. Outfall Locations and Dates of Industrial and Municipal Wastewater Effluent Samples.

Facility	Station	RM	Dates
Liberty Lake Sewer District WWTP	LIBLAKE	92.7	10/21– 22/2003 2/2 – 3/2004 4/26 – 27/2004
Kaiser Trentwood - Effluent	KaiserEff	86.0	10/21 – 22/2003 2/2 – 3/2004 4/26 – 27/2004
Kaiser Trentwood - Lagoon	KaiserLag	--	10/21 – 22/2003 2/2 – 3/2004 4/26 – 27/2004
Kaiser Trentwood - Below Filter	KaiserFilt	--	10/21 – 22/2003 2/2 – 3/2004 4/26 – 27/2004
Inland Empire Paper Company	Inland Emp	82.5	10/21 – 22/2003 2/2 – 3/2004 4/26 – 27/2004
City of Spokane WWTP	SPOKWWTP	67.4	10/21 – 22/2003 2/2 – 3/2004 4/26 – 27/2004

Samples were obtained by dipping a pre-cleaned glass container into the waste stream, either by hand or a stainless steel pole. Two-day composites included two quart grabs per day (morning and afternoon). A transfer blank was also collected during each round of sampling by pouring deionized water prepared at Manchester Environmental Laboratory into sample containers while on site. TSS samples were also collected as two-day grab composites at all facilities. Samples were placed on ice while in the field and maintained in coolers for transport with a chain-of-custody record.

Urban Stormwater

2004 Sampling

Three storm drains and one CSO were sampled during June 2004 (Table 11). Sampling was conducted by City of Spokane personnel during a runoff event produced by approximately 0.5 inches of rain in a 24-hour period. This event represented approximately one-half of the total precipitation for the month.

The storm-drain and CSO sites were selected by City of Spokane personnel based on recommendations by Ecology that the sites should be heavily developed with industrial land use

preferred, outfalls should be upstream of the Monroe St. Dam, and at least one should be a CSO outfall.

Table 11. Outfall Locations and Date of 2004 Storm Drain and CSO Samples.

Drain	Station	RM	Date
Mission Ave. and Perry St.	STMMISSBR	76.5	6/10/04
CSO at Erie St.	CSO34	75.8	
Superior St. near Cataldo St.	STMSUPOUT	75.7	
Washington St. Bridge	STMWASHBR	74.3	

The plan called for five storm drain/CSOs sampled during two runoff events, but a lack of precipitation, poor timing, and interference with other priorities of the City's stormwater sampling program precluded the successful completion of the plan.

2007 Contracted Sampling

In 2007 Ecology commissioned Parsons Inc. to conduct a Spokane stormwater study that sampled 14 sites including the four previously sampled storm drains/CSO. Stormwater sites were selected to be within the city limits and to discharge stormwater directly to the Spokane River. Parsons' subcontractor, TerraGraphics Environmental Engineering Inc., collected stormwater grab samples for PCBs and TSS during three storm events in May and June of 2007. The storm-event rainfall measured ranged from 0.29 to 0.86 inches and was preceded by more than four days of dry weather (Parsons, 2007).

Stormwater sampling locations for the Parsons study are described in Table 12.

Table 12. 2007 Stormwater Sampling Locations

Location ID	City Manhole Identifier	Latitude†	Longitude†	Location Description
STMWTR_ HWY291	0106436ST	47.73423	-117.507	Near the southwest corner of the intersection of Parkway Road and Ninemile Road (Hwy 291).
STMWTR_ 7TH	2000318ST	47.64898	-117.445	Next to light pole on southeast side of curb at intersection of 7th Street and Inland Empire. This is a combined sewer overflow (CSO 26).
STMWTR_ HSTREET	0400621ST	47.69031	-117.464	In the middle of H Street next to the alley north of Glass and south of Northwest Boulevard. This is a combined sewer overflow (CSO 07).
STMWTR_ COCHRAN	0501142ST	47.68353	-117.448	In the middle of Cochran Street, north of Grace Avenue west of TJ Meenach Drive Southern (and downstream) of two manholes.
STMWTR_ LINCOLN	0906615IN	47.66256	-117.425	Catch basin in sidewalk east of Lincoln Street next to Anthony's Restaurant, north of Post Street Bridge.
STMWTR_ CLARKE	1900330ST	47.65836	-117.439	Off north side of the curb of Clarke Street, east of Elm Street. This is a combined sewer overflow (CSO 24A).
STMWTR_ HOWARDBR	1000124ST	47.66485	-117.421	Northeast of Howard Bridge (walking bridge), just south of intersection with Mallon Avenue. In the middle of the trail. South of circle, approximately 12 feet east of catch basin, near map sign.
STMWTR_ UNION	1382924ST	47.66148	-117.392	In the middle of the street in front of the Union Gospel Mission, just south of intersection of Erie Street and Trent Avenue.
STMWTR_ RIVERTON	1800130ST	47.66751	-117.389	At the intersection of South Riverton Avenue and Desmet Avenue on the river side of the guardrail.
STMWTR_ GREENE	1680120ST	47.67772	-117.364	South of the Greene Street bridge, located on the sidewalk east of the bridge.
STMWTR_ WASHINGT	1100230ST	47.664	-117.418	North and west of Washington Street bridge. Located where the two paved walking trails converge. Previously named "stmwashbr."
STMWTR_ SUPERIOR	1300136ST	47.66579	-117.393	In the middle of Superior Street, south of Cataldo Avenue. Previously named "stmsupout."
STMWTR_ ERIECSO	0521966CD	47.66108	-117.393	South of Trent Avenue on Erie Street south of site 4217. Middle of three manhole covers in parking area of park. This is a combined sewer overflow (CSO 34). Previously named "CS034."
STMWTR_ MISSION	1400224ST	47.67227	-117.39	Northeast of the intersection of Perry Street and Mission Avenue near Avista. Previously named "stmmissbr."

† in decimal degrees
From Parsons, 2007.

Bottom Sediment

Surficial Deposits

Ecology collected surficial (top 2 cm) bottom sediments at several locations in the Spokane River, Little Spokane River, and a reference site. Surface sediment samples were collected from an Ecology boat using a 0.1 m² stainless steel van Veen or a 0.01 m² Petite Ponar grab sampler. Sediments from the Little Spokane were taken from the right bank using a pipe dredge. Sites were selected to assess the possibility of high concentrations of PCBs behind Monroe St. Dam, assess the longitudinal PCB concentration gradient in Lake Spokane, evaluate the potential of the Little Spokane River as a significant PCB source, and assess PCB concentrations in previously unexamined Spokane River reaches downstream of Lake Spokane.

The same reference site (Buffalo Lake) selected for an earlier bioassay survey of the Spokane Arm of Lake Roosevelt (Era-Miller, 2004) was used to provide reference sediments for the present 2003-07 study. It is located in a remote area of Okanogan County west of Spokane and receives contamination only through atmospheric deposition. An EPA study conducted during 2002 found low a PCB concentration (5.6 ng/g total PCBs) in largemouth bass fillets from Buffalo Lake (unpublished EPA data).

Table 13 lists locations for surficial sediment sampling. The riverbed behind the Monroe St. Dam in the vicinity of RM 76 and downstream of Little Falls Dam in the vicinity of RM 18-29 was composed almost entirely of gravel and cobble, and therefore no samples were collected.

Table 13. Locations and Dates of Surficial Sediment Samples.

Location	Station	RM	Date
Behind Monroe St./Upper Falls Dam	MonroeSed	74.9	4/14/2004
Lake Spokane (Long Lake)	LongLkUp	54.3	5/11/2004
	LongLkMid	44.3	11/4/2003
	LongLkLow	38.4	11/4/2003
Little Falls Pool	Littlefls	29.9	11/4/2003
Spokane Arm at Porcupine Bay	SPOK-1	12.6	11/6/2003
Little Spokane River	LitlSpokSed	2.3	12/10/2003
Buffalo Lake (reference)	BUFFALO REF	--	11/5/2003

Sediment Cores

Ecology collected sediment cores from the upper and lower reaches of Lake Spokane to assess trends in historic PCB deposition and to estimate sediment recovery rates (Table 14). Cores were collected using a Wildco 50-cm stainless steel gravity box corer fitted with a 13 cm by 13 cm (inner diameter) transparent acrylic liner.

Table 14. Locations and Dates of Sediment Cores.

Location	Station	RM	Date
Upper Lake Spokane	LONGUP2	49.2	6/9/2004
Lower Lake Spokane	LONGLOW2	36.0	11/4/2003

Fish and Crayfish Tissue

Ecology obtained fish and crayfish for PCB analysis from seven locations in the Spokane River from 2003 to 2005 (Table 15). For 2003 and 2004, the goal was to collect rainbow trout (>250 mm) and two size classes of largescale suckers (250-350 mm and <200 mm) at each site except Upriver Dam. Crayfish were collected at Upriver Dam due to interest in their possible accumulation of PCBs at the cleanup site. All biological data on specimens used for analysis are in Appendix E.

The goal for 2005 sampling was to provide high quality representative data to WDOH for use in a human health assessment and in reviewing the current fish consumption advisory stemming from data collected in 1999 and 2001. A secondary objective was to examine contaminant trends within the river system. Rainbow trout were not found during extensive efforts to capture them at Stateline and lower Lake Spokane. Largescale suckers were numerous at all sites except in the Ninemile reach where bridgelip suckers were the dominant species. The smaller size class of largescale suckers was not found at any of the sites sampled, even when various capture methods were employed.

Fish were collected primarily using Ecology's 16' Smith-Root electrofishing boat. Largescale suckers from Lake Spokane were captured using variable mesh gillnet sets on the lake bottom. Specimens were held in the vessel's live well and checked for species identification and desired length. Crayfish were collected using basket-cone style crayfish traps baited with cat food and set on the bottom overnight.

Fish selected for analysis were killed by a blow to the head. Each fish was given a unique identifying number, and its length and weight were recorded. The fish were individually wrapped in aluminum foil, put in plastic bags, and placed on ice for transport to Ecology headquarters, where the samples were frozen pending preparation of the tissue samples.

Crayfish were placed in a pre-cleaned 1 gallon glass jar and held on ice in coolers while in the field. Upon returning to Ecology headquarters, specimens were measured, weighed, and identified using an invertebrate species key. Following identification, specimens were returned to the jar and frozen until resection.

Table 15. Locations and Dates of Fish and Crayfish Samples.

Location	Station ID	RM	Latitude	Longitude	Species	Tissue	Dates
Near state line with Idaho	STATELINE-F	96.0	47.6981	-117.044	Largescale sucker	Whole body	7/14/04 [*]
	SPK 96	96.0	47.69832	-117.044			8/22/05 [†]
Near Plante Ferry Park	PLANTE-F	85.0	47.69459	-117.239	Rainbow trout	Fillet	9/15/03 [*]
					Largescale suckers	Gut contents	
	SPK 85	85.0	47.69498	-117.24	Rainbow trout Largescale suckers	Whole body	8/23/05 [†]
Behind Upriver Dam	Upriver Dam	80.3	47.6869	-117.325	Crayfish	Tail muscle	5/13/04 [*]
Mission Park	SPK 77	77.0	47.67655	-117.382	Mountain whitefish	Fillet	9/28/05-9/29/05 [†]
	SPK 75.2	75.2	47.66401	-117.404	Largescale sucker Rainbow trout	Whole body Fillet	9/28/05 [†]
Ninemile reservoir (near Seven Mile Bridge)	Spokane-F	61.7	47.7324	-117.51	Rainbow trout	Fillet	9/16/03 [*]
	NINEMILE-F	61.7	47.74299	-117.522	Rainbow trout	Gut contents	
	NINEMILE-F	61.7	47.74299	-117.522	Bridgelip sucker	Whole body Gut contents	7/13/04 [*]
	SPK 64.0	64.0	47.72043	-117.501	Rainbow trout	Fillet	9/29/05 [†]
					Mountain whitefish	Whole body	
					Bridgelip sucker	Fillet	
Upper Lake Spokane	SPK 55.6	55.6	47.80089	-117.549	Largescale sucker Smallmouth bass Mountain whitefish	Whole body Fillet Fillet	9/27/05 [†]
	SPK 55.2	55.2	47.80156	-117.558	Brown trout	Fillet	11/3/05 [†]
Lower Lake Spokane	SPK 40.1	40.1	47.83472	-117.737	Mountain whitefish	Fillet	11/3/05 [†]
		40.8	47.84152	-117.725	Smallmouth bass	Fillet	
	LONGLOW-F	39.4	47.82769	-117.745	Largescale sucker	Whole body	7/13/04-7/14/04 [*]

^{*} Sampling conducted in support of the present study. See Jack et al. (2003) for Quality Assurance Project Plan.

[†] Serdar and Johnson (2006).

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Sample Preparation

Sample containers and holding times for 2003-2005 are shown in Table 16. The fish and crayfish tissue preparation techniques used are described in Appendix F. See Parsons (2007) for sample preparation, analytical methods, and data quality information for stormwater samples collected in 2007.

Analytical Methods

All PCB congener samples and percent lipid in tissue were analyzed at Pace Analytical Services, Inc., Minneapolis, MN. PCB Aroclors, TOC in sediments, and TOC, DOC, and TSS in water were analyzed at Manchester Environmental Laboratory. SPMD preparation and dialysis was done at Environmental Sampling Technologies (EST), St. Joseph, MO. Radioisotope analysis of sediment cores was done at Teledyne Brown Engineering, Knoxville, TN. Grain size analysis was done at Analytical Resources, Inc., Tukwila, WA.

Table 16 shows analysis methods and reporting limits for sample media.

Table 16. Preparation Methods, Analytical Methods, and Reporting Limits for the Spokane River Samples.

Sample Media	Parameter	Preparation Method	Analytical Method	Reporting Limits
Semipermeable Membrane Device (SPMD)	PCB Congeners	Dialysis and ampulization - EST SOP	GC/HRMS, EPA Method 1668A	100 ng/4 ML dialysate (per congener) translates to approx. 0.1 - 1 pg/l (per congener)
Water	PCB Congeners	--	GC/HRMS, EPA Method 1668A	100 pg/l (per congener)
	TSS	--	EPA Method 160.3	1 mg/L
	TOC	--	EPA Method 415.1	1 mg/L
	DOC	--	EPA Method 415.1	1 mg/L
Sediment (Suspended particulate matter and surficial sediment)	PCB Congeners	Soxhlet extraction	GC/HRMS, EPA Method 1668A	0.05 ng/g (per congener)
Sediment	PCB Congeners	Soxhlet extraction	GC/HRMS, EPA Method 1668A	0.05 ng/g (per congener)
	TOC (104 °C)	--	Combustion	0.1%
	Grain size	--	Sieve and Pipet	±0.5% for each fraction
Sediment (Core)	PCB Aroclors	Soxhlet extraction	GC/ECD, EPA Method 8082	1 - 25 ng/g (per Aroclor)
	TOC (104 °C)	--	Combustion	0.1%
	Pb-210	--	Gamma detection	--
Tissue	PCB Congeners	Soxhlet extraction	GC/HRMS, EPA Method 1668A	0.01 - 0.05 ng/g (per congener)
	% lipids	--	Gravimetric	0.1%

SOP = Standard operating procedure.

Data Quality Assessment

Ecology's Manchester Laboratory reviewed the chemical data for this project. For results generated by Manchester, final data review was performed by the unit supervisor or an analyst experienced with the method. Manchester chemists performed the review for analytical work sub-contracted to commercial laboratories. Quality assurance and quality control at Manchester are described in the *Lab Users Manual* <http://aww.ecologydev/programs/eap/forms/labmanual.pdf> (Ecology Intranet).

Manchester prepared written case narratives assessing the quality of all data collected. These reviews include a description of analytical methods and an assessment of holding times, initial and continuing calibration and degradation checks, method blanks, surrogate recoveries, internal standard recoveries, matrix spike recoveries, laboratory control samples, and laboratory duplicates. The reviews and the complete Manchester data reports are available from the author on request.

A Quality Assurance Project Plan (Jack, 2003) established measurement quality objectives (MQOs) for accuracy, bias, and reporting limits. To determine if MQOs were met, the project lead compared results on field and laboratory quality control samples to the MQOs. To evaluate whether the reporting limit targets were met, the results were examined for non-detects and to determine if any values exceeded the lowest concentration of interest. Based on these assessments and a review of the laboratory data packages and Manchester's data verification reports, the data were either accepted, accepted with appropriate qualifications, or rejected and re-analyzed or re-sampled where possible.

The precision and accuracy of the 2003-2005 data reported here can be gauged from results on laboratory duplicates, field replicate samples, and standard reference materials, detailed in Appendix G. The relative percent difference (RPD) between duplicate (split) and replicate (separately collected) samples was 20% or better for PCBs in effluents, fish tissue, and sediment. Greater variability was encountered in analyzing PCBs in SPMD extracts, 9-55% RPD. Results from analyzing PCB congeners in a sediment standard reference material agreed within 13% of certified values, on average.

Results and Discussion

Dissolved PCBs in Spokane River Water

Ancillary water quality data collected in concert with SPMD deployments are shown in Table 17. Organic carbon concentrations were low at all sites. DOC constituted approximately 92% of the TOC on average. TSS concentrations were generally ≤ 3 mg/L with higher values (4-10 mg/L) occurring in February and April.

With a few exceptions, average temperatures were similar at all mainstem locations during each deployment. Stateline and Lake Spokane were approximately 1.5°C warmer than other sites in October, but Stateline temperatures were slightly colder in February. Lake Spokane temperatures were also the warmest among mainstem sites in February. At Upriver Dam, bottom and middle water column temperatures were nearly identical.

Dissolved PCB concentrations determined from analyzing the SPMD membranes are shown in Table 18. A summary of the PCB residues accumulated in the membranes (raw data) is in Appendix C.

Concentration estimates for dissolved total PCBs ranged from 34 pg/l (parts per quadrillion) at Stateline during February (2004) to a maximum of 656 pg/l at lower Lake Spokane during October (2003). PCBs were composed primarily of tri- through heptachlorobiphenyl congeners. Spokane River total PCBs showed a fairly consistent trend of increasing concentrations moving downstream. Generally, dissolved total PCB concentrations were comparatively low at Stateline and Upriver Dam (34-145 pg/l), intermediate at Monroe St. and Ninemile (76-305 pg/l), and highest at Lake Spokane (78-656 pg/l). Total PCB concentrations in the Little Spokane River were 118-178 pg/l. The PCB mixture in the Little Spokane was enriched in octa, nona, and deca homologues compared to the mainstem Spokane River, suggesting a difference in sources.

There was evidence of seasonal differences in total PCB levels, with concentrations highest during October and lowest during February (Figure 11). Total PCB measured during October and April appeared similar at all reaches except for a large divergence at Lake Spokane. One possible reason for the much higher PCB concentration in Lake Spokane in October is the fall breakdown of stratification, which allowed bottom water enriched in PCBs to mix with the upper water column. This is consistent with SPMD findings for Upriver Dam, discussed below.

Table 17. Ancillary Parameters at SPMD Sites (mg/L).

Station Name	Sample Number	Collection Date	DOC		TOC		TSS		Mean Temp. (°C)
Stateline	3408971	10/1/03	1.1		1.3		1	U	14.4
	3448107	10/29/03	1.1		1.2		2		
	4058111	1/28/04	1.4		1.3		1	U	3.2
	4094040	2/24/04	1.2		1.3		1		
	4164041	4/14/04	1.2		1.6		3		10.8
	4208134	5/12/04	1		1.2		2		
Upriver Dam	3408966/72*	10/1/03	1.2		1.5		2		12.7
	3448108	10/29/03	1		1.2		1		
	4058112	1/28/04	1.2		1.4		1		3.5
	4094044/5*	2/25/04	1.2		1.3		2		
	4164042/3*	4/14/04	1.6		1.7		3		10.8
	4208135	5/12/04	1		1.1		2		
UPRIVER BOT	--	10/1/03	--		--		--		12.7
	--	10/29/03	--		--		--		
	--	1/28/04	--		--		--		3.6
	4094046	2/25/04	1.1		1.3		2		
	4164044	4/14/04	1.3		1.4		3		9.8
	4208136/7*	5/12/04	1.1		1.1		2		
Monroe St	3408968	10/2/03	1	U	1	U	1	U	12.0
	3448109	10/29/03	1	U	1.1		1		
	4058113	1/28/04	1	U	1.1		2		4.0
	4094047	2/25/04	1.2		1.2		1		
	4164045	4/14/04	1.4		1.3		3		10.8
	4208138	5/12/04	1	U	1.3		2		
Ninemile1	3408967	10/1/03	1	U	1	U	1	U	12.3
	3448110	10/29/03	1.1		1.3		2		
	4058114/5*	1/28/04	1.2		1.3		2		--
	4094041	2/24/04	1.4		1.8		4		
Ninemile2	4164046	4/14/04	1.4		1.4		6		10.8
	4208139	5/12/04	1		1.1		2		
LongLkLow	3408969	10/2/03	1.1		1.1		2		14.4
	3454120	11/4/03	1	U	1	U	2		
	4164040	4/13/04	1.1		1.5		4		10.8
	4208133	5/11/04	1.1		1.3		3		
Tum Tum	4058117	1/29/04	1		1.1		2		4.5
	4094043	2/24/04	2.1		2.6		4		
LitlSpokR	3408970	10/2/03	1	U	1	U	1		14.4
	3448111	10/30/03	1	U	1	U	2		
LitlSpokBr	4058116	1/29/04	1	U	1	U	8		4.5
	4094042	2/24/04	2.7		2.2		10		
	4164047	4/14/04	1.3		1.7		7		10.8
	4208140	5/12/04	1.1		1	U	5		

*Mean of replicate analysis.

U: The analyte was not detected at or above the reported result, equivalent to <1.

Stateline: Spokane River at the Idaho state line just downstream of Interstate 90 bridge.

Upriver Dam: Spokane River upstream of Upriver Dam.

UPRIVER: Spokane River upstream of Upriver Dam, 2 feet from bottom of riverbed.

Monroe St: Spokane River upstream of Monroe Street Dam.

Ninemile1: Spokane River at Riverside State Park.

Ninemile2: Spokane River downstream of boat launch at Plese Flats

LongLkLow: Lower Lake Spokane.

Tum Tum: Lake Spokane near Tum Tum.

LitlSpokR: Little Spokane River at State Route 291 bridge.

Table 18. SPMD Dissolved PCB Concentrations Grouped by Homologues (pg/l), 2003-2004.

Station Name	Sample Number	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl	9-Cl	10-Cl	Total PCBs
October 2003												
Stateline	474155	0.4	1.5	11	15	56	19	7.9	2.4	0.0	0.0	113
Upriver Dam	474156/7*	0.7	5.5	25	26	32	10	3.7	0.0	0.0	0.0	103
UPRIVER BOT	474158	0.4	5.0	31	48	43	13	4.8	0.7	0.0	0.0	145
Monroe St	474159	0.6	8.6	32	60	65	42	18	3.0	0.0	0.0	231
Ninemile1	474160	0.3	13	63	61	95	49	21	3.1	0.0	0.0	305
LongLkLow	474161	0.7	15	59	269	195	74	32	9.3	2.3	0.0	656
LitlSpokR	474162/3*	0.2	1.0	12	27	33	16	12	11	6.4	0.0	118
February 2004												
Stateline	194130	0.0	0.0	1.8	4.6	14	8.9	5.0	0.0	0.0	0.0	34
Upriver Dam*	194131/2*	0.1	0.6	5.6	12	15	3.7	19	0.0	0.0	0.0	56
UPRIVER BOT	194133	0.0	0.3	10	40	22	4.1	0.8	0.0	0.0	0.0	78
Monroe St	194134	0.0	1.0	9.5	21	20	13	11	0.0	0.0	0.0	76
Ninemile1	--	--	--	--	--	--	--	--	--	--	--	--
Tum Tum	194135	0.0	1.4	12	24	18	8.9	13	0.1	0.0	0.0	78
LitlSpokBr*	194136/7*	0.1	0.4	9.1	35	51	16	12	13	6.9	0.0	143
April 2004												
Stateline	208134	0.0	0.3	8.0	17	60	32	27	2.1	0.0	0.0	145
Upriver Dam	208135	0.0	0.0	2.1	16	14	6.6	4.6	0.9	0.0	0.0	45
UPRIVER BOT*	208136/7*	1.8	1.0	24	78	57	17	11	0.5	0.0	0.0	191
Monroe St	208138	0.1	1.8	21	53	80	40	31	4.0	0.0	0.0	231
Ninemile2	208139	0.5	2.6	25	57	68	40	28	3.9	0.0	0.0	225
LongLkLow	208133	0.6	6.0	25	94	84	34	16	3.3	0.0	0.0	263
LitlSpokBr*	208140/1*	0.4	0.8	18	37	53	19	23	14	10	3.1	178

*Mean of replicate analysis.

Note: Reporting limits were variable, 0.1 – 10 pg/l.

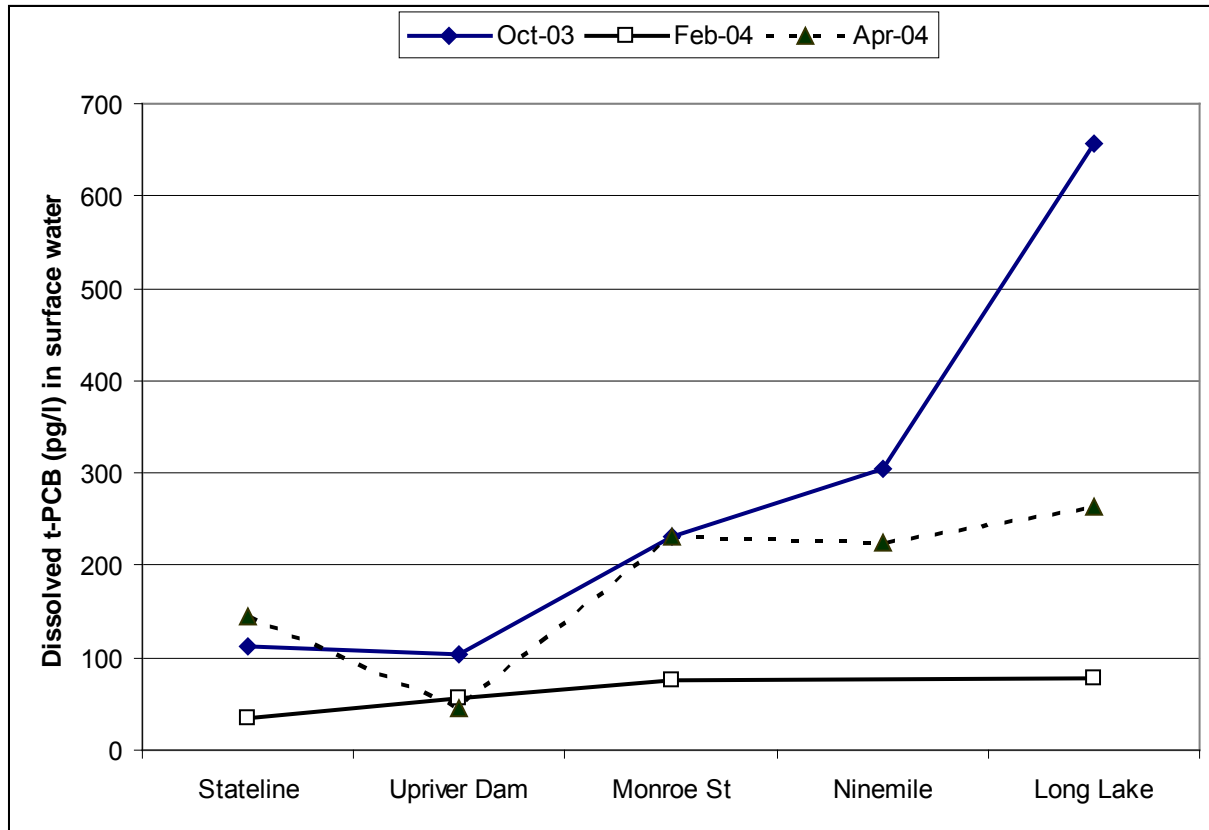


Figure 11. Dissolved Total PCBs in the Spokane River, 2003-2004.

Dissolved PCBs at Monroe Street, Ninemile, and lower Lake Spokane did not meet (exceeded) Washington State's human health water quality criterion of 170 pg/l. During October, the total PCB concentrations at these sites ranged from 231 to 656 pg/l. In April, the concentration range was 231 to 263 pg/l. The Little Spokane River was at the criterion in April (178 pg/l).

The February total PCB concentrations were similar among reaches and low compared to other months. Lower concentrations during this deployment may have been more a result of colder temperatures which reduce the SPMD sampling rate but is not accounted for in calculations used to translate SPMD PCB residues to surface water concentrations (see Appendix C). This may also explain the consistent total PCB concentrations in the Little Spokane River, since February and April temperatures at this location were 2-3°C warmer. Simple flow dilution does not explain the differences among deployments since Spokane River discharge was highest during April (325 m³/s at Spokane), lowest during October (49 m³/s), and intermediate during February (114 m³/s).

One objective of the SPMD sampling at the Upriver Dam cleanup site was to assess PCB levels at different depths. Samplers deployed 1-2 feet from the bottom had consistently higher concentrations than those at mid-depth (12-13 feet above bottom, Figure 12). The difference was pronounced in April when the bottom sample was four times the mid-column sample, even though the temperature was 1°C lower (and thus a slightly lower sampling rate) at the bottom. Temperatures at both depths were identical during the other deployments.

At the time of sampling, higher PCB concentrations near the bottom were expected at this site which has PCB contaminated sediments that had yet to undergo state-directed cleanup (see previous Upriver Dam discussion). Although the high level of organic carbon in some of the PCB contaminated sediments theoretically sequesters PCBs, some diffusion to the water column occurs which was captured by the near-bottom SPMDs.

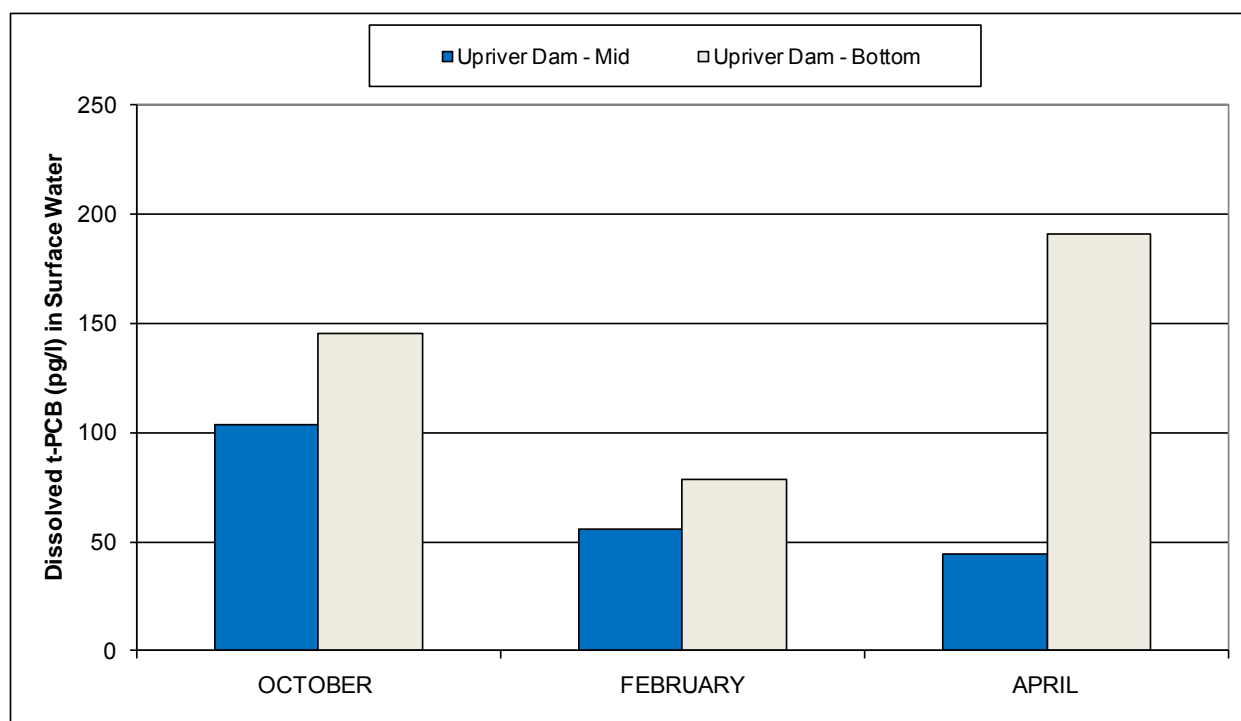


Figure 12. Dissolved Total PCBs at Mid-depth and Near the Bottom at Upriver Dam.

PCBs in Spokane River Suspended Particulate Matter

PCBs were measured in suspended particulate matter (SPM) and whole water from the Spokane River at Harvard Rd., Plante Ferry, and Ninemile during three two-day events in October-November 2003. For each sample collection (Oct 20-21, Oct 28-29, and Nov 3-4), a generator run pump was used to draw water up to a large centrifuge. Whole water samples were pumped to a sample container immediately upstream of the centrifuge. Ancillary water quality parameters included TOC, DOC, and TSS (Appendix D). TOC and DOC values were generally ≤ 1 mg/L. TSS averaged 1 mg/L at Harvard Road and Ninemile and 2 mg/L at Plante Ferry.

In SPM, PCBs were composed primarily of tetra-, penta-, and hexachlorobiphenyl congeners (Table 19). [Compared to dissolved PCBs which were composed primarily of tri- through heptachlorobiphenyl congeners. See previous discussion on dissolved results for the Spokane River.] Total PCB concentrations in suspended particles from Ninemile (69 ng/g, parts per billion) were an order of magnitude higher than those upstream (7.1-9.6 ng/g). The low TSS concentrations during all three sampling events indicate that differences in total PCB concentrations were not due to sediment entrainment.

For the most part, detection limits in the whole surface water samples were not low enough to afford a useful comparison with the SPM data. No PCBs were detected in the whole water samples collected at Harvard Rd. or Plante Ferry at the 110 pg/l level, and only a low concentration (130 pg/l) of dichlorobiphenyl congeners was detected at Ninemile (Table 19). This is an unusual finding considering the relatively low concentration of this homologue group in SPM and SPMDs.

Earlier (1994) SPM sampling by Ecology (1995) at Plante Ferry yielded much higher PCB concentrations (220 ng/g) using the same collection methods as the present 2003-07 study. Although that result was obtained using an Aroclor rather than congener analysis, river conditions were similar, TSS was low (<1 mg/L), and the sampling site was nearly identical.

To examine the proportion of solid and dissolved phase PCB concentrations in the Spokane River, the following partition formula was applied to the SPM data:

Equation 3. ***Fraction of dissolved PCB*** =
$$\frac{1}{(1+(f_s*f_{oc}*K_{oc}))}$$

Where:

- f_s = fraction of solid in water.
- f_{oc} = fraction of organic carbon in the solid phase.
- K_{oc} = sediment-water partition coefficient normalized for organic carbon.

This formula assumes that PCBs are in equilibrium between the solid and dissolved phases, and the proportion in each phase is governed by the amount of solids in the water and the organic carbon content of the solid material. K_{oc} , the sediment-water partition coefficient normalized for organic carbon, is a field or laboratory-derived constant for each chemical. Values for f_s were from TSS measurements (1 or 2 mg/L; i.e., f_s = 0.000001 or 0.000002). Values for f_{oc} (0.15) and K_{oc} (449,000) are from EPA (1994) and DiToro et al. (1991), respectively, and are the same values used by Ecology (1995) to calculate a dissolved PCB concentration in water from earlier sampling.

Based on sediment-water partitioning, approximately 94% of the PCBs are in the dissolved phase. Dissolved total PCB concentration for Harvard Rd. and Plante Ferry are 142 and 105 pg/l, respectively, similar to results derived from SPMD deployments at Stateline and Upriver Dam during the same period (\approx 110 pg/l). The theoretical dissolved concentration of total PCBs was 1,020 pg/l at Ninemile, more than three times the concentration measured with SPMDs (305 pg/l) during October (in Table 18).

Table 19. PCB Concentrations Grouped by Homologues in Suspended Particulate Matter (ng/g, dw) and Whole River Water Collected at the Centrifuge Inlet (pg/l) During Three Sampling Events from October to November 2003.

	Station	Sample Number	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl	9-Cl	10-Cl	Total PCBs
Suspended Particulate Matter													
Spokane R at Harvard Rd	Harvard	3438100	<0.0 9	0.11	0.51	0.96	2.91	3.40	1.39	0.32	<0.0 9	0.09	9.60
Spokane R at Plante Ferry Park	PLANTEFRY	3448100	<0.0 5	0.09	0.41	1.34	2.49	1.98	0.70	0.08	<0.0 5	0.05	7.09
Spokane R at Riverside State Park	NINEM SPM	3454105	<0.0 7	0.39	3.71	12.9	24.6	18.6	6.30	1.71	0.39	0.15	68.8
Whole Water Centrifuge Inlet													
Spokane R at Harvard Rd	Harvard	3438100	REJ	<111	<11 1	<111	<111	<111	<111	<111	<111	<122	<111
Spokane R at Plante Ferry Park	PLANTEFRY	3448100	<109	<109	<10 9	<109	<109	<109	<109	<109	<109	<120	<109
Spokane R at Riverside State Park	NINEM SPM	3454105	<108	130	<10 8	<108	<108	<108	<108	<108	<108	<119	130

Detected values are in green highlight.

<: The analyte was not detected at or above the reported result.

REJ: Data are unusable for all purposes.

Figure 13 shows the two-day whole water PCB concentrations estimated from the suspended matter data and illustrates the relative importance of the dissolved PCB component, at least during low-flow conditions. Results also suggest that the analysis of whole surface water samples collected during particulate matter sampling underestimated actual PCB concentrations.

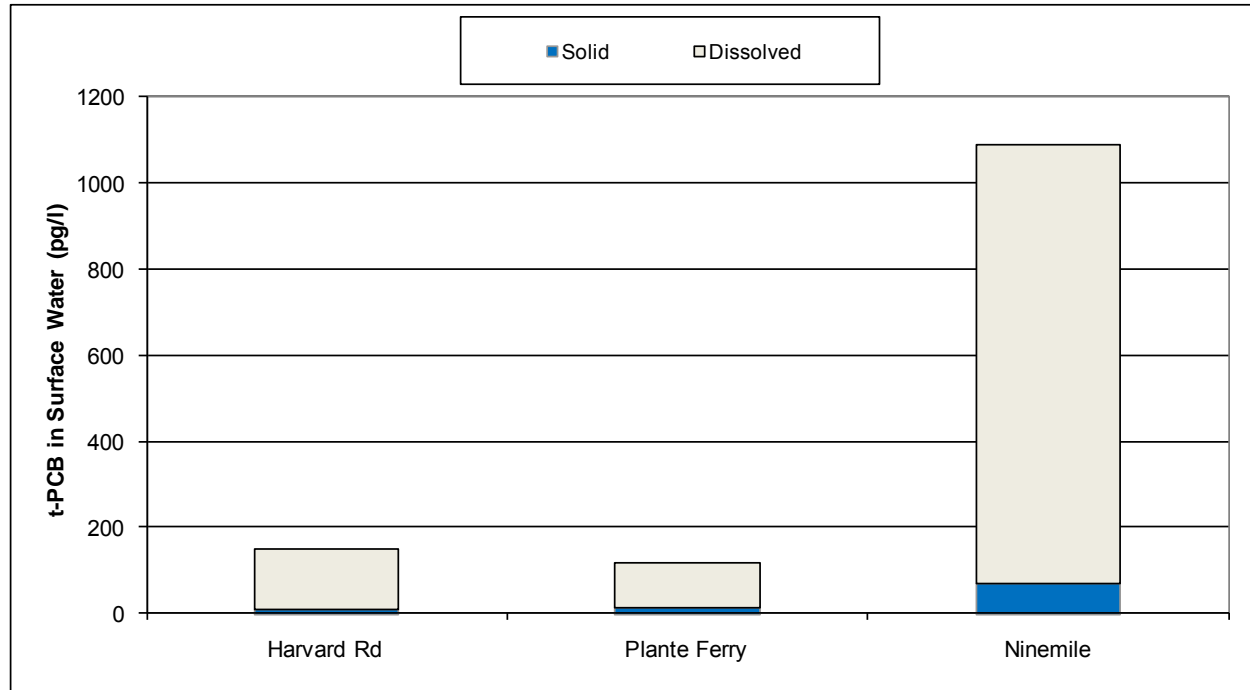


Figure 13. Measured Particle-Bound PCB Concentrations and Theoretical Dissolved PCB Concentrations Based on Suspended Particulate Matter Collected by Three 2-Day Centrifugation Sampling Events of Spokane River Water in October and November 2003.

PCBs in Industrial and Municipal Effluents Discharged to the Spokane River

In late 2003, Kaiser Trentwood installed a black walnut shell filtration system for their process wastewater discharge. Results of 2004-2005 effluent sampling showed an order of magnitude decrease in PCB concentrations and loads compared to 2001, presumably due to the filter and other facility management improvements. Table 20 shows the results of effluent PCB monitoring by Kaiser in 2004-2005 (unpublished).

Table 20. Kaiser Trentwood Effluent Concentrations of Total PCBs (Kaiser, 2005).

Source	Date	Total PCBs (pg/l)*	Effluent Flow (ML/day)	PCB Load to River (mg/day)
Kaiser Trentwood	6/25/04	1,170	63.9	75
	7/7/04	1,230	64.6	79
	7/23/04	1,340	66.2	89
	8/9/04	914	62.4	57
	4/20/05	669	56.2	38
	5/7/05	928	56.1	52
	5/19/05	1,370	59.7	82
	6/11/05	971	56.5	55
	6/14/05	1,130	55.4	63

*sum of detected congeners.

PCBs monitored by Ecology in effluents from four industrial and municipal facilities during three periods – October 2003, February 2004, and April 2004 – are shown in Table 21. Descriptions of the station names and sampling dates were listed in Table 10.

Spokane WWTP was the only facility where PCBs were detected in effluent during all three sampling collections, with an average PCB concentration of 940 pg/l.

Total PCBs in the Kaiser Trentwood effluent were generally <110 pg/l except during October when 330 pg/l was detected on 10/21/2003. Total PCBs were undetected at the 100 pg/l detection limit the following day. Samples from the treatment lagoon at Kaiser showed much higher PCBs (110 – 7,400 pg/l), but these concentrations were reduced substantially by the bed filtration system prior to discharge.

Liberty Lake WWTP had variable concentrations, as did Inland Empire to a lesser degree. Total PCB concentrations at Liberty Lake WWTP were an order of magnitude higher during April than during October and February, while Inland Empire had only one sample with PCBs detected, 670 pg/l total PCBs in October.

Overall, it appears that PCB concentrations in the effluents of the four facilities have decreased substantially since previous sampling. The smallest decrease occurred at the Spokane WWTP where 2003-04 average concentrations were about one-half those during 2001. However, the bulk of this apparent decrease may be due to higher detection limits used for the 2003-2004 samples compared to earlier samples. Effluent samples analyzed by Golding (2002) and SAIC (2003a) typically had detection limits <5 pg/l for individual congeners, and nearly all detected congeners were found at concentrations <100 pg/l. Therefore, the 2003-2004 results are likely all biased low due to the omission of these detections.

The reason for the relatively high level of monochloro-biphenyls in the 2004 Liberty Lake and Spokane WWTP replicate samples is unknown. The poor agreement between the Spokane WWTP replicate samples suggests contamination either from the field or laboratory. These values do not have a significant impact on the PCBs loading scenarios presented later in the report.

Table 21. PCB Concentrations Grouped by Homologues in Industrial/Municipal Effluent (pg/l).

Station Name	Sample ID	TSS mg/L	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl	9-Cl	10-Cl	Total PCBs
October 2003													
LIBLAKE	3434025	7	<98	161	<98	<98	<98	<98	<98	<98	<98	<98	161
KaiserEff	3434020	1	<100	100 J	228	<100	<100	<100	<100	<100	<100	<110	328 J
KaiserEff	3434023	1	<101	<101	<101	<101	<101	<101	<101	<101	<101	<112	<101
KaiserLag	3434021	3	<102	292 J	911	1,350	<102	<102	<102	<102	<102	<112	2,550 J
KaiserFilt	3434022	1	<100	167 J	104	<100	<100	<100	<100	<100	<100	<110	271 J
Inland Emp	3434026	5	<101	670	<101	<101	<101	<101	<101	<101	<101	<111	670
SPOKWWTP	3434027	6	<99	143	<99	112	218	<99	<99	<99	<99	<108	473
February 2004													
LIBLAKE	4064113	31	<111	<111	<111	<111	<111	<111	<111	<111	<111	<122	<111
KaiserEff	4064105	1	<112	<112	<112	<112	<112	<112	<112	<112	<112	<123	<112
KaiserEff Rep.	4064106	1	<106	<106	<106	<106	<106	<106	<106	<106	<106	<116	<106
KaiserEff	4064107	1	<109	<109	<109	<109	<109	<109	<109	<109	<109	<119	<109
KaiserLag	4064110	5	<106	422	2,580	3,720	647 J	<106	<106	<106	<106	<117	7,370
KaiserFilt	4064109	1	<109	<109	307	125 J	<109	<109	<109	<109	<109	<120	432 J
Inland Emp	4064111	9	<109	<109	<109	<109	<109	<109	<109	<109	<109	<120	<109
SPOKWWTP	4064112	10	<108	<108	<108	123	259	122	<108	<108	<108	<119	504
April 2004													
LIBLAKE	4188205	43	999 NJ	<112	<112	265	<112	<112	<112	<112	<112	<123	1,260 NJ
KaiserEff	4188198	1	<112	<112	<112	<112	<112	<112	<112	<112	<112	<112	<112
KaiserEff	4188199	1	<107	<107	<107	<107	<107	<107	<107	<107	<107	<107	<107
KaiserLag	4188202	1	<104	112 J	<104	<104	<104	<104	<104	<104	<104	<104	112 J
KaiserFilt	4188201	1	<106	<106	<106	<106	<106	<106	<106	<106	<106	<106	<106
Inland Emp	4188203	2	<112	<112	<112	<112	<112	<112	<112	<112	<112	<112	<112
SPOKWWTP	4188204	5	<102	<102	<102	342	588	329	<102	<102	<102	<113	1,260
SPOKWWTP Rep.	4188206	6	865 NJ	<107	<107	360	826	358	<107	<107	<107	<117	2,410 NJ

Detected values are in green highlight.

<: The analyte was not detected at or above the reported result (U or UJ).

NJ: There is evidence that the analyte is present. The associated numerical result is an estimate.

J: The analyte was positively identified. The associated numerical value is an estimate.

PCBs in Stormwater Discharged to the Spokane River

Stormwater sampling during the 2003-04 PCB source assessment study was conducted by City of Spokane personnel during one runoff event on June 10, 2004. Only four locations were sampled, although the sampling plan proposed more sites and storm events. Samples were collected from manholes nearest the outfalls draining the particular stormwater conveyance systems.

Due to the limited data from 2004, a second and larger set of stormwater samples was collected in the spring of 2007 by Parsons, a consultant hired by Ecology. Locations are shown in Figure 14. Results from both the 2004 and 2007 efforts are presented in Tables 22 to 26. The location IDs that correspond to the location descriptions were shown in Tables 11 and 12.

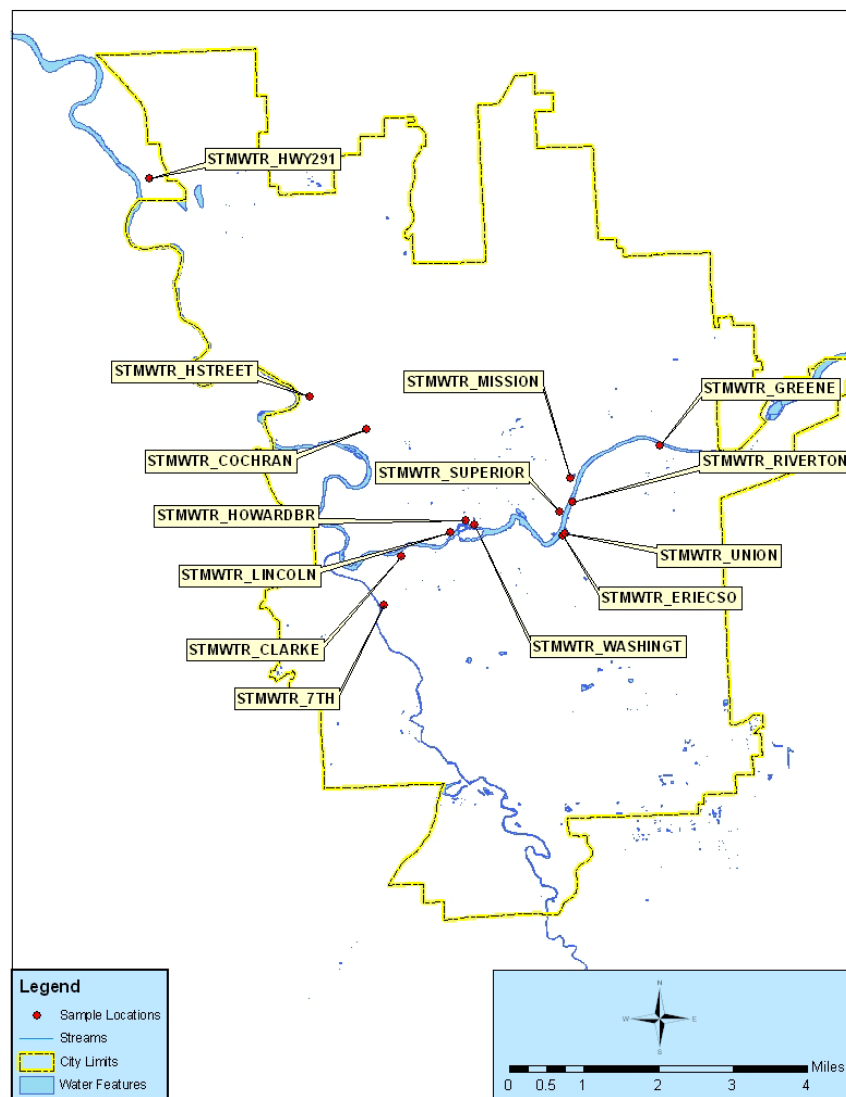


Figure 14. Stormwater Basins in the City of Spokane Sampled for PCBs During 2007 by Parsons.

Table 22. June 10, 2004 Stormwater PCB Concentrations Grouped by Homologues (pg/l).

Location ID*	Sample Number	TSS (mg/L)	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl	9-Cl	10-Cl	Total PCBs
Stmwtr_Mission (STMMISSBR)	4254001	58	<117	<117	117	5,490	28,800 J	19,200	6,660	1,600	283	254	62,400 J
Stmwtr_ErioeCSO (CSO 34)	4254000	126	<111	<111	685	3,120	10,200	28,500	32,400	7,800	678	<123	83,400
Stmwtr_Superior (STMSUPOUT)	4254003	26	<102	<102	<102	843	1,920	1,270	749	120	<102	<112	4,900
Stmwtr_Washingt (STMWASHBR)	4254002	91	<113	<113	285	2,560	8,380 J	5,290 J	2,530	690	198	<124	19,900 J

Detected values are in green highlight.

* Location ID in parentheses is presented for access to data in EIM. The Location IDs correspond to Table 12, which is the ID given for the 2007 stormwater sampling.

<: The analyte was not detected at or above the reported result (U or UJ).

J: The analyte was positively identified. The associated numerical value is an estimate.

Table 23. May 2, 2007 Stormwater PCB Concentrations Grouped by Homologues (pg/l).

Location ID*	Sample ID	TSS (mg/L)	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl	9-Cl	10-Cl	Total PCBs
HWY291	07184210	19	76	78	45	483 J	572	408	446	70	<20	<20	2180 J
7 TH (CSO 26)	07184211	22	<80	<80	<80	<80	713 J	575	120	<80	<80	<80	1410 J
HSTREET (CSO 7)	07184212	63	<20	120	135	855 J	1,380	973	768	190	54	48	4520 J
COCHRAN	07184213	155	85	578	953	2,430 J	5,770	4,440	2,890	813	293	<20	18,250 J
LINCOLN	07184214	8	<20	<20	88	622 J	1,130	556	315	56	44	<20	2810 J
CLARKE (CSO 24A)	07184215	4	<80	<80	<80	<80	<80	<80	<80	<80	<80	<80	<80 ¹
HOWARDBR	07184216	7	<20	102	194	849 J	734	408	309	29	27	42	2700 J
UNION	07184217	67	75	1,960	8,500	21,990	27,660	39,350	42,050	24,860	1,570	160	168,160
RIVERTON	07184218	27	23	336	919	6,570	17,200	10,050	6,050	1,900	99	<20	43,140
WASHINGT	07184221	26	57	295	408	1,700 J	2,800	1,330	1,110	514	82	<20	8,290 J
SUPERIOR	07184222	43	61	440	859	4,970 J	21,340	10,830	2,620	996	84	33	42,230 J
ERIECSO (CSO34)	07184223	40	115	2,960	13,650	29,140	48,120	85,070	78,890	20,190	2,000	296	280,430
MISSION	07184224	34	<100	319 J	381 J	2,990 J	9,720	6,690	2,220	452	<100	<100	22,770 J
SUPERIOR-Replicate	07184225	306	<100	342 J	527	2,350	9,250	6,670	1,410	690	<100	<100	21,230 J
SUPERIOR-Replicate	07184226	27	65	496	971	2,620	6,720	5,310	1,740	1,310	40	<20	19,260

Detected values are in green highlight.

*: In EIM these Locations IDs have the prefix STMWTR_; CSO number in parentheses is not part of the EIM Location ID.

¹: The Clarke 07184215 Total PCB was revised from 0.062 to <80, post publication in the 2007 Parsons Report. The online report reflects the change.

<: The analyte was not detected at or above the reported result (U or UJ).

J: The analyte was positively identified. The associated numerical value is an estimate.

Table 24. May 21, 2007 Stormwater PCB Concentrations Grouped by Homologues (pg/l).

Location ID*	Sample ID	TSS (mg/L)	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl	9-Cl	10-Cl	Total PCBs
HWY291	07214210	8	110	105 J	<40	66 J	231	<40	<40	<40	<40	<40	512 J
7 TH (CSO 26)	07214211	7	<40	158	51 J	296	342	144	<40	<40	<40	<40	991
HSTREET (CSO 7)	07214212	41	<40	137 J	<40	315 J	801 J	514	305	108	<40	<40	2,179 J
COCHRAN	07214213	12	43 J	135 J	<40	125 J	275 J	95 J	46 J	<40	<40	<40	719 J
LINCOLN	07214214	3	<40	164 J	<40	132 J	353 J	187	<40	<40	<40	<40	836 J
CLARKE (CSO 24A)	07214215	2	<40	101 J	<40	124	<40	<40	<40	<40	<40	<40	225 J
HOWARDBR	07214216	3	<40	122 J	57 J	302 J	317 J	42 J	<40	<40	<40	<40	839 J
UNION	07214217	18	142	373 J	645	1,795 J	3,006 J	4,325	4,631	1,121	62 J	<40	16,099 J
RIVERTON	07214218	14	52 J	<40	47 J	422 J	856 J	997	1,511	356	<40	<40	4,240 J
GREENE	07214219	38	54 J	233 J	828	2,367 J	3,033 J	2,254	2,238	403	<40	<40	11,409 J
WASHINGT	07214221	11	159	132 J	<40	<40	395 J	247	49 J	<40	<40	<40	981 J
WASHINGT-Replicate	07214225	8	108	136 J	<40	169 J	396 J	132	<40	<40	<40	<40	939 J
WASHINGT-Replicate	07214226	9	74 J	80 J	<40	156 J	402 J	239	65 J	<40	<40	<40	1,017 J
SUPERIOR	07214222		196	110 J	<40	155 J	304 J	202	185	<40	<40	<40	1,152 J

Detected values are in green highlight.

*: In EIM these Locations IDs have the prefix STMWTR_

<: The analyte was not detected at or above the reported result (U or UJ).

J: The analyte was positively identified. The associated numerical value is an estimate.

Table 25. June 5, 2007 Stormwater PCB Concentrations Grouped by Homologues (pg/l).

Location ID*	Sample ID	TSS (mg/L)	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl	9-Cl	10-Cl	Total PCBs
HWY291	07234710	6	<40	<40	<40	<40	98 J	143	<40	<40	<40	<40	241 J
7 TH (CSO 26)	07234711	26	150	121	91 J	702 J	2,708 J	2,382	1,059	382	64 J	48 J	7,707 J
HSTREET (CSO 7)	07234712	46	<40	<40	<40	<40	422 J	266 J	62 J	<40	<40	<40	749 J
COCHRAN	07234713	298	65 J	552	724	2,458 J	5,257	6,301	2,535	1,078	518	110	19,598 J
LINCOLN	07234714	51	<40	215	378	1,187 J	3,163 J	2,818	852	495	255	61 J	9,423 J
CLARKE (CSO 24A)	07234715	92	<40	108	72 J	452 J	1,725 J	1,628	591	196	94 J	<40	4,867 J
HOWARD BR	07234716	67	<40	605	4,404	4,662	2,366 J	1,722	773	210	111	86 J	14,940 J
HOWARD BR-Replicate	07234725	63	<40	528	4,393	4,158	2,549 J	1,222	627	121	122	93 J	13,813 J
HOWARDBR-Replicate	07234726	46	<40	433	3,591	3,302	1,760 J	1,410	566	130	79 J	123	11,393 J
UNION	07234717	65	49 J	511	2,387	5,037	12,488	39,653	36,975	9,056	602	44 J	106,802
RIVERTON	07234718	82	<40	200	500	1,465 J	3,824 J	6,735	5,309	1,222	124	<40	19,380 J
GREENE	07234719	117	<40	295	1,770	3,631	5,599	9,275	5,463	1,315	232	43	27,622
WASHINGT	07234721	158	<40	216	404	1,947 J	2,726 J	2,489	681	318	171	80 J	9,031 J
SUPERIOR	07234222	55	<40	116	109	742 J	1,451 J	1,622	593	227	53 J	<40	4,912 J
ERIECSO (CSO34)	07234223	159	62 J	582	2,094	4,987	10,768	28,081	19,456	6,027	568	62 J	72,686
MISSION	07234224	30	<40	120	152	897 J	3,131 J	3,593	1,884	446	90 J	<40	10,311 J

Detected values are in green highlight.

*: In EIM these Locations IDs have the prefix STMWTR_

<: The analyte was not detected at or above the reported result (U or UJ).

J: The analyte was positively identified. The associated numerical value is an estimate.

Summary statistics for PCB concentrations in City of Spokane stormwater samples from 2004 and 2007 are shown in Table 26. Stormwater PCB concentrations ranged over two orders of magnitude in both data sets from 2004 and 2007. Individual total PCB concentrations varied widely from <80 to 280,000 pg/l in the 2007 Parsons study, and from 4,900 to 83,400 pg/l in 2004.

Table 26. Summary Statistics for Total PCB Concentrations in Spokane Stormwater (pg/l).

Statistic	Stormwater Sampling	
	Ecology in 2004	Parsons in 2007
minimum	4,900	240
10th	9,400	777
25th	16,150	1,118
mean	42,650	23,023
median	41,150	8,000
75th	67,650	19,290
90th	77,100	42,867
95th	80,250	101,684
maximum	83,400	280,430

Parsons provided an in-depth review of the 2007 data in their report (Parsons, 2007). They concluded that:

- Stormwater basins CSO 34 and Union Street showed the highest average concentrations for the three events.
- Total PCB concentrations showed a direct correlation with TSS.
- Sources of PCBs are similar in the stormwater systems, with the exception of the Howard Bridge site. The greater relative abundance of less chlorinated PCBs at Howard Bridge may indicate the presence of a different source.

Post publication of the Parsons report, Union Street was found to drain to the CSO34 (Erie Street) system. Their relative drainage areas are 109 and 1,951 acres, respectively. Thus, Union Street, at <6% of the CSO 34 area, may be largely responsible for the high PCB levels detected at CSO 34.

The Clarke 07184215 total PCB result was revised post publication of the Parsons (2007) report from 0.062 to <80 pg/l.

A wide range of PCB homologues was detected in Spokane stormwater (Tables 22-25) and in particulate samples from the Spokane River (Table 19). A similar homologue range was seen in Spokane River sediment samples (see Table 30). In contrast, a relatively narrow group of dichloro through pentachlorobiphenyl homologues was found in industrial and municipal effluents (Table 21). This finding, coupled with the loading analysis that follows, supports a conclusion that stormwater is a significant PCB source to the Spokane River.

Stormwater Discharges

Streamflow data were not collected during stormwater sampling. Therefore the discharge was estimated using calculations based on rainfall. The average annual stormwater discharge predicted by the Simple Method (www.stormwatercenter.net) was calculated by Parsons (2007). Briefly, the Simple Method uses the equation:

$$\text{Equation 4. } R = P * P_j * R_v$$

where R is annual runoff (inches), P is annual rainfall (inches), P_j is the fraction of annual rainfall events that produce runoff (assumed 0.9), and R_v is a runoff coefficient.

In this method, the runoff coefficient is calculated based on impervious area in the subwatershed (I_a). Watershed imperviousness is a reasonable predictor of R_v (Schueler, 1987), with the relationship best defined as:

$$\text{Equation 5. } R_v = 0.05 + 0.9I_a$$

Geographical data were provided by the City of Spokane Wastewater Management Department. Annual rainfall was estimated to be 18 inches in Spokane, based on data from Ecology's Eastern Washington Stormwater Manual Precipitation Maps (Ecology, 2004 www.ecy.wa.gov/biblio/0410076maps.html). A value of 0.9 was used as the fraction of runoff.

The first step for developing flow estimates using the Simple Method was to determine the area draining to each of the sampling locations. To do so, a shapefile of stormwater boundaries provided by the City of Spokane was merged with the shapefile of areas contributing stormwater to the various CSOs (also provided by the City of Spokane) in a geographic information system. Figure 15 presents the combined stormwater-CSO boundaries for the entire city.

The second step was to determine the impervious areas. Pervious surfaces were determined in each drainage area based on 2007 geographic data. The total impervious area contributing was calculated as the sum of transportation and off-street impervious areas. Percent impervious for all the stormwater basins in the City of Spokane ranged from roughly 12 to 54% for the basins with any development (Parsons, 2007). This stormwater assessment did not take the Census-defined urban areas nor the Urban Growth boundary into account. The Spokane city limits were defined by the 2005 city boundary.

The total PCB average for each sampling station, as well as the calculated impervious fraction, area, and runoff, are shown in Table 27.

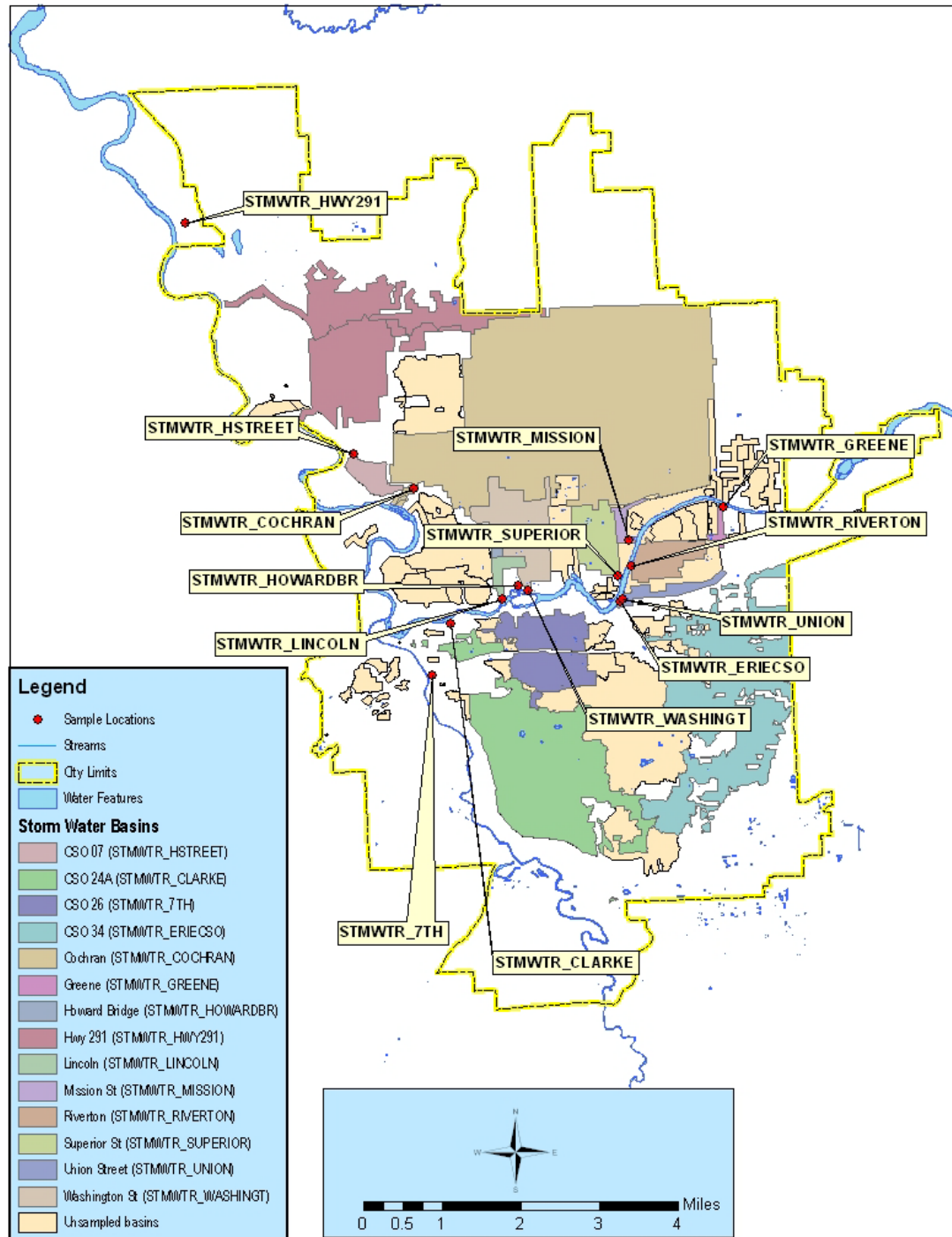


Figure 15. Stormwater Basins in the City of Spokane, Parsons, (2007).

Table 27. Total PCB Results, Impervious Fraction, and Runoff for Spokane Stormwater Basins.

Location_ID ¹	Total PCB (ng/L) ²	Impervious Fraction	Drainage Area (acre)	Annual Runoff Volume (in) ³
Sampled Stormwater Basins (High CSO Load Scenario)				
Above Monroe St Dam				
GREENE	19.5	0.365	34	6.1
MISSION	16.5	0.277	55	4.8
RIVERTON	22.3	0.217	233	4
SUPERIOR	17.8	0.376	294	6.3
UNION	97	0.323	109	5.5
ERIECSO (CSO 34)	177	0.24	2,060 ⁴	4.3
WASHINGT	4.05	0.417	465	6.9
HOWARDBR	8.74	0.407	57	6.7
Below Monroe St Dam				
LINCOLN	4.36	0.544	69	8.7
CLARKE (CSO 24A)	2.56	0.267	1,863	4.7
7 TH (CSO 26)	3.38	0.439	609	7.2
COCHRAN	12.9	0.274	5,164	4.8
HSTREET (CSO 7)	2.49	0.247	121	4.4
HWY291	0.978	0.248	1,578	4.4
Totals			12602	79
29 Un-Sampled Stormwater Basins (Low CSO Load Scenario)				
Average Conc.	23			
Totals		varied	4652	147

Green shading represents CSO basins.

¹ In EIM these Locations IDs have the prefix STMWTR_; CSO number in parentheses is not part of the EIM Location ID.

² Average of all the samples collected in the 2007 Parsons study; the PCB average was updated by Ecology.

³ Calculated for stormwater basins only, using Equations (6) and (7) and an annual rainfall amount of 18 inches.

⁴ Includes Union area (109 acres).

PCB stormwater concentrations were found to be related to TSS concentrations in the Parsons study. TSS concentrations were substantial in stormwater (2-298 mg/L, Tables 22-25). Based on the high octanol-water partitioning coefficients (K_{ow}) for PCBs and the high TSS concentrations, it can be assumed that most of the PCBs were adsorbed to the solids fraction in stormwater. Approximately 85%-95% of the PCBs were estimated to be bound to the solid phase (i.e., attached to the suspended sediment) when the partitioning formula Eq. 3, described previously, was applied and an organic carbon fraction of 0.05 used. If this is the case, the suspended sediment carried in stormwater would have average dry weight t-PCB concentrations ranging from approximately 150 to 1,000 ng/g, or about two to 15 times the levels seen in suspended particulate matter in the Spokane River at Ninemile.

PCBs in Spokane River Bottom Sediments

Bottom sediment sampling site locations and dates are shown in Table 28. These sites were selected to investigate the possibility of PCB enriched sediments behind Monroe St. Dam, assess the longitudinal PCB concentration gradient in Lake Spokane, evaluate the potential of the un-surveyed Little Spokane River as a significant PCB source, and measure PCB concentrations in previously sampled Spokane River reaches downstream of Lake Spokane.

Table 28. Bottom Sediment Locations and Sampling Dates.

Station Location	Sample Name	RM	Dates
Spokane River above Monroe St.	MonroeSed	74.8	4/14/04
Upper Lake Spokane	LongLkUp	54.3	5/11/04
Middle Lake Spokane	LongLkMid	44.3	11/4/03
Lower Lake Spokane	LONGLKLOW	38.4	10/2/03 11/4/03 4/13/04
Spokane River above Little Falls Dam	Littlefls	29.9	11/4/03
Spokane River at Porcupine Bay	SPOK-1	11.3	11/06/03
Little Spokane River above SR291	LitlSpokSed	1.1	12/10/03
Buffalo Lake	BUFFALO REF	--	11/5/03

Due to the lack of bulk fine-grained deposits in the Spokane River, sampling was limited to a smaller number of sites than originally planned. Sampling the fine-grained sediment deposit behind Upriver Dam was deemed unnecessary due to the intensive investigation and cleanup being completed at this site.

Grain size composition and PCBs in surficial (top 2 cm) sediments from various Spokane River locations and one reference site (Buffalo Lake) are shown in Tables 29 and 30, respectively.

Table 29. Grain Size in Bottom Sediments (%).

Sample Name	Sample Number	Sand	Gravel	Silt	Clay
MonroeSed	04168149	47.1	52	0.8	0.0
LongLkUp	04208147	22	0.1	73.6	4.3
LongLkMid	03454111	3.6	0	76.3	20.2
LONGLKLOW	03454112/4*	7.0	0.1	59.1	34.0
Littlefls	03454113	88.2	0	9.4	2.3
SPOK-1	03458100	9.7	0	66.5	23.8
LitlSpokSed	03504060	84	0.2	13	2.8
BUFFALO REF	03458103	23.3	0.3	25.4	50.9

*Mean of replicate analysis.

Table 30. PCB Concentrations Grouped by Homologues in Surficial (top 2 cm) Bottom Sediments (ng/g, dw).

Station Name	Sample Number	TOC (%)	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl	9-Cl	10-Cl	Total PCBs
MonroeSed	4168149	0.36	<0.01	<0.01	0.04	0.15	3.00J	1.79	0.90	0.24J	0.05J	<0.02	6.17J
LongLkUp	4208147	2.8	0.17J	0.90	5.99	16.1	13.1J	8.52J	3.50	1.06	0.23	0.12	49.7J
LongLkMid	3454111	2.98	<0.24	0.30	3.05	7.31	5.54	5.23	1.76	0.86	0.27	0.08	24.4
LONGLKLOW	3454112/4*	2.81	0.09J	0.37	2.80	8.49	6.89	4.22	2.23	0.94	0.22	0.08	26.3
Littlefls	3454113	0.61	<0.05	0.10	0.24	0.52	0.62	0.35	0.05	<0.05	<0.05	<0.05	1.90
SPOK-1	3458100-S	1.71	<0.05	0.20	0.72	3.61	3.08	1.59	0.89	0.28	0.07	<0.05	10.4
LitlSpokSed	3504060	0.85	<0.05	<0.05	0.06	0.16	0.31	0.24	0.25	0.75	0.30	<0.05	2.06
BUFFALO REF	3458103-S	8.24	<0.05	0.06	0.07	0.30	0.82	0.81	0.30	0.12	0.23	0.16	2.88

*Mean of replicate analysis.

Detected values are in green highlight.

<: The analyte was not detected at or above the reported result.

J: The analyte was positively identified. The associated numerical value is an estimate.

Concentrations ranged from 50 ng/g total PCB at upper Lake Spokane to 1.9 ng/g at Little Falls. Upper Lake Spokane sediments have total PCB concentrations similar to suspended particulate matter concentrations at Ninemile, suggesting that this material is deposited in this reach. Surficial sediment PCB levels from the lower and middle reaches of Lake Spokane were one-half those in the upper reach.

The river sediments at Monroe St. had low PCB concentrations (6.2 ng/g total PCB) as did the Little Spokane River (2.1 ng/g) and Little Falls. The low concentrations probably reflected a lack of organic carbon-enriched fine material in these reaches. When PCB concentrations among sites were compared on an organic carbon normalized basis, the Lake Spokane stations retained the same relative PCB levels, Little Falls and the Little Spokane River were comparatively low, and Monroe St. total PCB concentrations were as high as those from upper Lake Spokane (Figure 16).

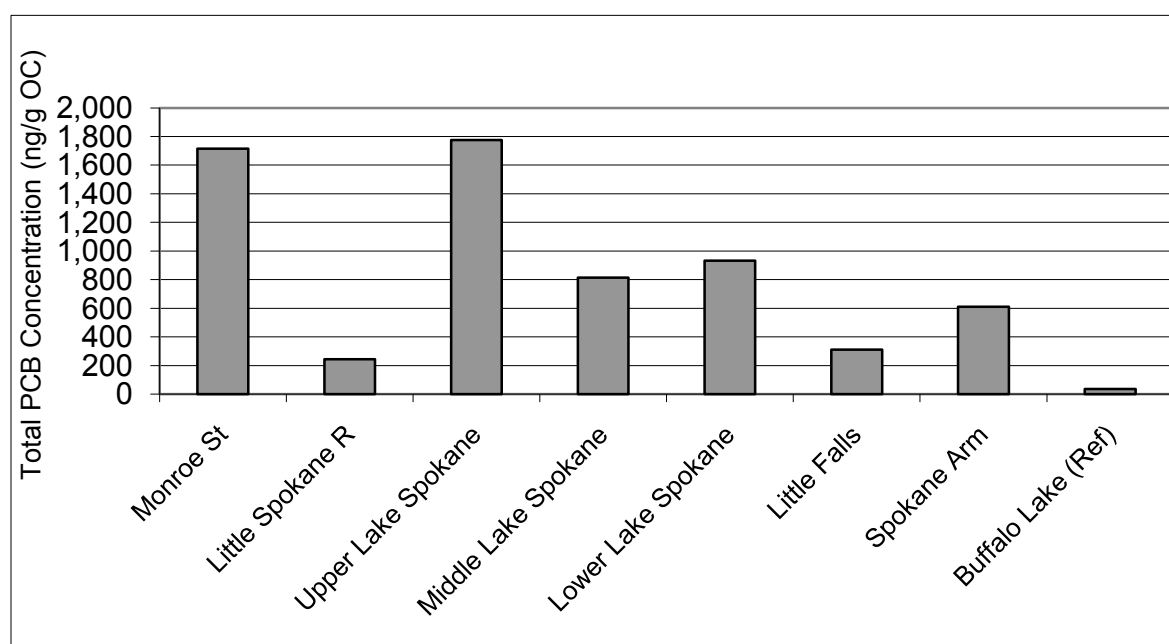


Figure 16. Surficial (Top 2 cm) Sediment PCB Concentrations in Spokane River and Little Spokane River Sediments Normalized to Organic Carbon (Buffalo Lake is a reference location).

TOC-normalized total PCB concentrations at Monroe St. and Upper Lake Spokane sediments were elevated 50 times the reference sediment from Buffalo Lake. Middle and lower Lake Spokane sediments were one-half that elevation. Little Spokane River and Little Falls sediments were more than nine times above PCBs in the reference sediments, while Spokane Arm (Porcupine Bay) levels were 18 times higher.

Temporal trends in sediment PCBs are difficult to establish due to the higher reporting limits in the Aroclor analysis of previous studies. For instance, Johnson and Norton (2001) found TOC-normalized total PCB concentrations of 400, 740, and 3,800 ng/g organic carbon at upper, middle, and lower Lake Spokane, respectively, but few Aroclors were detected and reporting limits were often >10 ng/g. In 1993, Ecology found 1,400 ng/g organic carbon at lower Lake

Spokane, using essentially the same analysis and near the same location (Ecology, 1995). Spokane Arm (Porcupine Bay) sediments from the same survey showed 770 ng total PCB/g organic carbon, representing the only other comparable data for sediments.

To more closely examine the historical record of PCB deposition in Spokane River sediments, PCBs were analyzed at various depths in a 30-cm core collected in upper Lake Spokane and in a 44-cm core from lower Lake Spokane. Table 31 shows total PCB concentrations at various depths in each core. Figures 17 and 18 show the chronology of PCB deposition based on radionuclide (^{210}Pb) decay in sediments (Appleby and Oldenfield, 1978).

Table 31. Total PCB Concentrations in Sediment Cores from Upper and Lower Lake Spokane (ng/g, dw).

Station/Sample ID	Depth (cm)	TOC (%)	Total PCB
LONGUP2			
04268382	0-1	2.82	8
04268383	1-2	2.38	14
04268384	3-4	2.27	16
04268385	5-6	1.81	16
04268386	7-8	1.94	19
04268387	9-10	1.79	33
04268388	11-12	1.85	32
04268389	14-15	1.85	28
04268390	24-25	2.01	51
04434079	28-29	1.87	32
04268391	29-30	2.58	30
LONGLOW2			
04268372	0-1	3.08	28
04268373	1-2	2.76	75
04268374	3-4	2.83	42
04268375	5-6	2.48	40
04268376	7-8	2.41	27
04268377	9-10	2.36	32
04268378	11-12	2.69	54
04268379	14-15	2.74	59
04268380	24-25	2.70	233
04268381	34-35	2.70	1,000
04434078	41-42	2.70	701

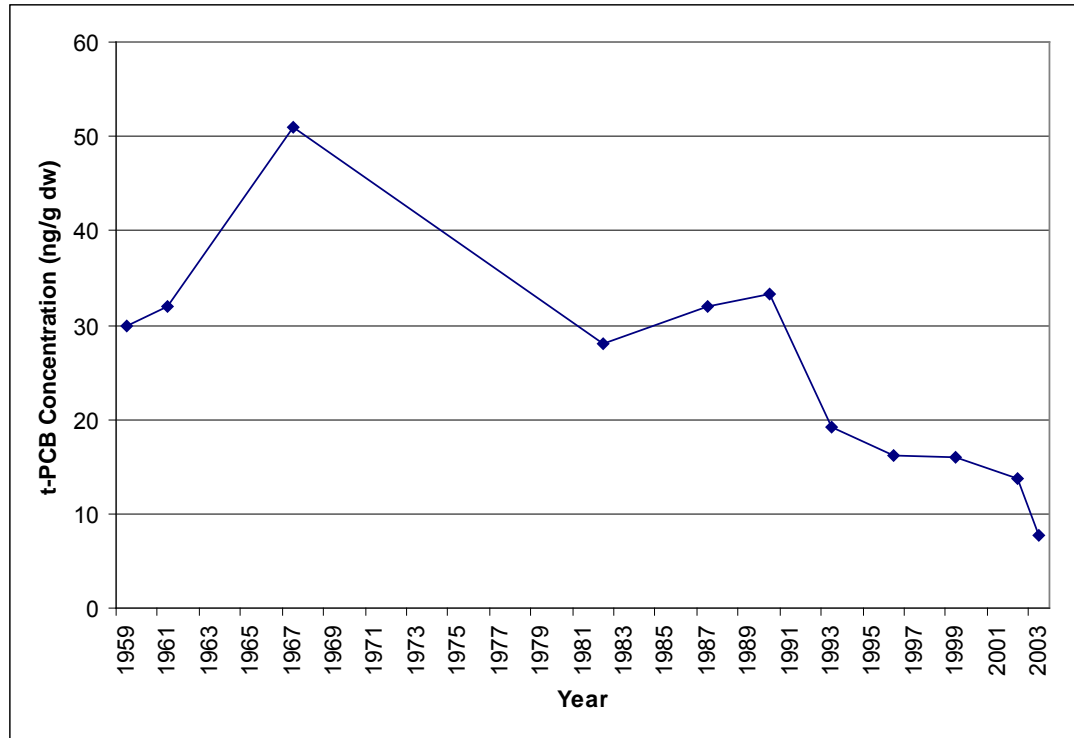


Figure 17. Chronology of PCB Concentrations in Upper Lake Spokane Sediments.

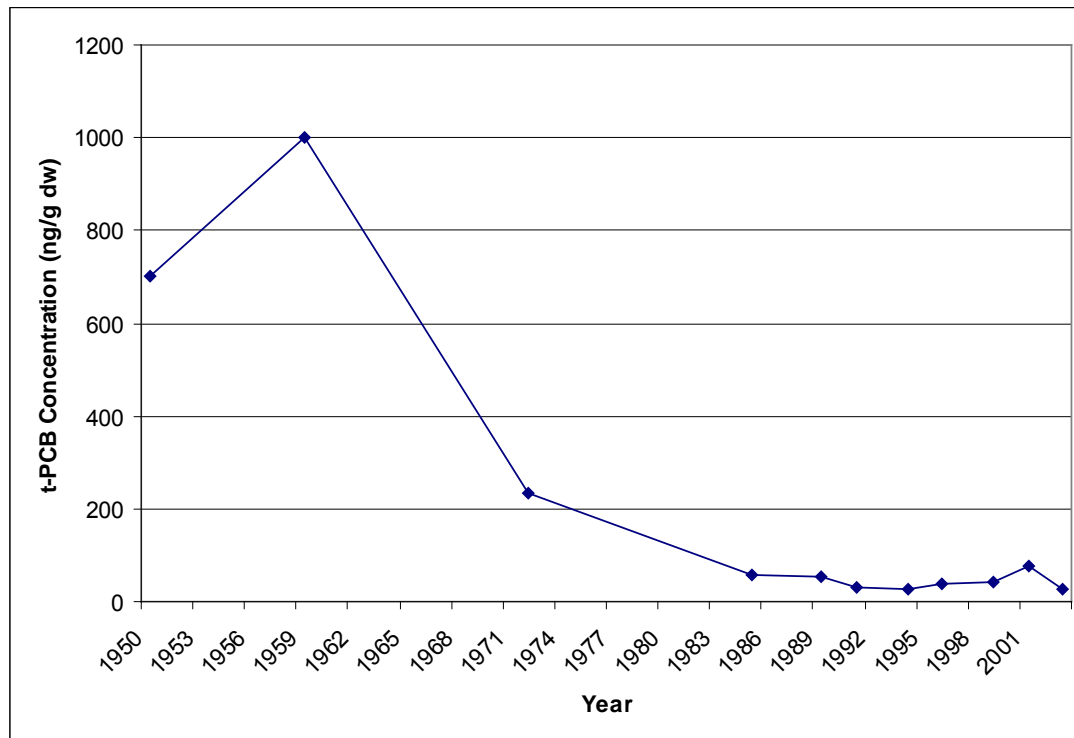


Figure 18. Chronology of PCB Concentrations in Lower Lake Spokane Sediments.

The sediment core from upper Lake Spokane was not as deep as desired due to coarser material preventing maximum corer penetration, and therefore PCB history could only be traced to circa 1959. The PCB profile showed a declining trend from 1959 to 2003, with a 1967 peak (51 ng/g), nearly coinciding with peak domestic PCB production in 1970.

The shape of the PCB profile from lower Lake Spokane had similarities to the upper lake. The peak occurred earlier with 1,000 ng/g circa 1959, but no horizons deposited between 1959 and 1972 were analyzed for PCBs, raising the possibility that the peak PCB concentration in this core was more than 1,000 ng/g and may have occurred later than 1959. PCB concentrations in sediment deposits have leveled off significantly in the past two decades, a pattern that has been observed at other locations in Washington (e.g., Serdar, 2003).

Cores from upper and lower Lake Spokane differ vastly in PCB levels, with peak years showing at least a 30-fold higher concentration at the lower lake. Lower Lake Spokane had post-peak total PCB concentrations 2-5 times higher than those deposited the same years in the upper lake, except during the early 1990s when PCB levels were nearly identical.

The surficial sediments and those normalized to TOC show upper Lake Spokane has higher PCBs. However, the sediment core samples and other studies indicate lower Lake Spokane historically had higher PCBs. This most likely has to do with the complex sedimentation history of the Lake Spokane Dam reservoir and sedimentation patterns from the tributaries to the lake.

The differences in PCB concentrations between upper and lower Lake Spokane and the apparent variability in PCB concentrations in upper lake sediments indicate that these locations receive sediments at proportionally different rates over time and possibly from different sources. The high level of PCBs historically deposited in the lower lake most likely originate from PCB contamination sources in and around Spokane, whereas the upper lake sediments are probably diluted with comparatively clean sediments from the Little Spokane River and Latah Creek, the latter providing large volumes of clean sediment (Johnson and Norton, 2001; SCCD, 2002).

The ^{210}Pb profile in the lower lake shows a steady input of newly formed material and little perturbation of sediments, while upper lake sediments appear to contain older material near the surface, presumably delivered from Little Spokane River and Latah Creek, and an inconsistent decay profile suggesting physical disturbance. Future analysis of upper lake sediments should be conducted with caution and consideration for the dynamics of sedimentation in this reach.

PCBs in Spokane River Fish

2003-2004

As part of the PCB source assessment, several species of fish were collected from multiple locations in the Spokane River from the state line through Lake Spokane. Table 32 shows concentrations of PCBs in rainbow trout fillets and in gut contents. Male rainbow trout from Plante Ferry had a somewhat higher PCB concentration than females, even though female fish were larger on average (391 vs. 363 mm). One possible explanation for the difference in concentrations at this location is that female fish may have mobilized PCBs along with lipids to egg production, since all female trout from this location were gravid. However, lipid content was nearly identical between sexes, suggesting other factors at play. Ninemile rainbow trout had slightly lower PCB concentrations than Plante Ferry possibly due to the smaller length (311 vs. 377 mm), exposure history, or lower lipids (1.3 vs. 1.7%) on average.

The Ninemile rainbow trout, having been analyzed individually, offer an opportunity to examine some of the factors determining PCB levels in tissue for fish collected from this location. Upon initial inspection, it appears that sex differences play a large role in PCB concentrations since females have twice the average PCB levels compared to males. However, the median age of the female fish was three years versus one year for the male fish, and the females were 20% longer on average. Another possible factor is the origin of the specimens; the larger females were all wild fish while the majority of male specimens were hatchery-raised based on the pattern of scale checking (John Sneva, WDFW, written communication). Differences in PCB levels of wild versus hatchery fish also may be due to foraging habits or prey selection.

PCB concentrations in rainbow trout gut contents were approximately 15%-30% those in tissue. Many of the specimens collected at both Plante Ferry and Ninemile were engorged with filamentous plant material. This material holds insects and other aquatic organisms, which are digested while the plant material remains undigested. Aquatic organisms extracted from Ninemile trout stomachs were mostly Corixidae (water boatman) adults, Chironomidae larvae, and Trichoptera larvae (probably Hydropsychidae). The gut contents of Plante Ferry rainbow trout were not examined closely, but casual observation suggested that contents were similar to Ninemile specimens; and PCB concentrations were similar as well. Crayfish or crayfish parts were also observed in the guts of some Plante Ferry trout.

Table 33 shows congener and total PCB concentrations (sum of detected congeners) in suckers analyzed whole and in gut contents. Crayfish from the Upriver Dam cleanup site are also included in Table 33. Suckers were composited by size to assess growth dilution as a potential factor in PCB concentrations. Growth dilution occurs when a fish grows faster than the accumulation rate of the contaminant of concern, lowering the contaminant concentration as the fish size increases.

Table 32. 2003-2004 PCB Concentrations in Rainbow Trout from Plante Ferry and Ninemile (ng/g, ww)

Station-Tissue	Sample ID	Composite	Sex	Lipid	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl	9-Cl	10-Cl	Total PCB
Fillet															
PLANTE-F	4188308	Y	M	1.7%	0.004N	0.03	0.14	7.15	13.4	9.08J	10.2J	0.83	0.15J	0.02	40.9 J
	4188309	Y	F	1.7%	0.01J	0.06J	0.09	5.13J	6.35J	9.97J	5.82J	0.81	0.11	0.02	28.4 J
mean=															34.7
Ninemile (WSTMP) ²	084281	N	M	1.5%	<0.02	0.02	0.14	1.81	3.29	3.08	1.12	0.25	<0.02	<0.02	9.7
	084282/308 *	N	F	2.7%	0.02	0.03	1.01	6.45	19.8	20.4	6.45	1.73	0.16	0.02	56.0
	084283	N	M	1.3%	<0.02	0.03	0.13	2.35	5.04	4.25	1.41	0.26	0.03	<0.02	13.5
	084284	N	M	1.9%	<0.02	0.03	0.72	4.96	13.1	10.3	4.44	0.83	0.08	<0.02	34.4
	084285	N	F	1.1%	<0.02	<0.02	0.08	4.58	16.9	19.4	7.74	1.88	0.30	0.04	50.9
	084286	N	M	1.0%	<0.02	0.02	0.12	2.18	4.43	3.65	1.04	0.14	0.02	<0.02	11.6
	084287	N	M	0.4%	<0.03	<0.03	0.53	1.73	4.87	3.68	1.24	0.30	<0.03	<0.03	12.3
	084288	N	M	1.9%	<0.03	0.04	1.03	3.09	6.17	4.86	1.66	0.40	<0.03	<0.03	17.3
	084289	N	F	0.7%	<0.02	0.02	0.61	3.80	12.8	15.4	7.06	2.44	0.19	0.03J	42.4
	084290	N	M	3.3%	<0.02	0.04	1.70	9.48	31.2	19.0	10.7	2.20	0.15	<0.02	74.5
	084291	N	F	2.5%	<0.02	0.04	1.36	7.33	19.5	16.3	5.95	1.25	0.16	0.03	51.9
	084292	N	M	2.0%	<0.02	0.03	1.13	6.27	17.0	13.6	5.56	1.04	0.12	<0.02	44.8
	084293	N	M	1.8%	<0.02	0.03	0.39	3.75	9.98	8.96	3.23	0.65	0.09	<0.02	27.1
	084294	N	M	1.0%	<0.02	0.03	0.14	1.86	4.00	2.65	0.79	0.23	<0.02	<0.02	9.7
	084295	N	M	0.6%	<0.02	0.03	0.14	2.70	4.91	4.59	1.94	0.27	0.03	<0.02	14.6
	084296	N	M	0.4%	<0.02	0.03	0.11	2.20	4.18	2.72	1.16	0.25	0.02	<0.02	10.7
	084298	N	M	0.9%	<0.02	0.03	0.72	2.55	4.90	4.94	1.94	0.46	0.03	<0.02	15.6
	084299	N	M	0.2%	<0.02	0.03	0.07	2.62	7.16	4.67	1.84	0.39	0.02	<0.02	16.8
	084301	N	M	1.5%	<0.02	0.03	0.89	5.72	13.6	15.7	5.37	1.59	0.16	0.02	43.2
	084302	N	M	0.8%	<0.02	0.03	0.77	3.04	6.48	6.48	2.76	0.53	0.03	<0.02	20.1
	084303	N	F	0.9%	<0.02	0.03	0.60	3.29	9.30	10.7	3.28	1.35	0.11	0.02	28.7
	084304	N	M	0.3%	<0.02	<0.02	0.23	1.58	4.05	3.15	0.97	0.38	0.02	<0.02	10.4
	084305	N	M	0.5%	<0.03	0.04	0.55	1.89	4.29	3.35	1.66	0.33	<0.03	<0.03	12.1
	084306	N	M	1.6%	<0.02	0.03	1.00	4.32	11.9	12.8	3.38	1.03	0.10	<0.02	34.6
mean of males =															22.8
mean of females =															46.0
mean overall =															27.6
Gut Contents															
PLANTE-F	4188311	Y			0.01N	0.03	0.06	0.11	1.77	0.97J	0.99J	0.14	0.02N	<0.02	4.1 J
NINEMILE-F	4188310	Y			<0.01	0.03	0.04	0.06	2.42	2.02J	1.35	0.21	0.03N	<0.01	6.2 J

¹ These Ninemile fish were collected under the station name "Spokane-F" as part of a concurrent WSTMP study and were analyzed as individuals.

*Mean of replicate analysis.

Detected values are in green highlight.

U: The analyte was not detected at or above the reported result.

J: The analyte was positively identified. The associated numerical value is an estimate.

NJ: There is presumptive evidence that the analyte is present. The associated numerical result is an estimate.

Table 33. 2003-2004 PCB Concentrations in Suckers and Crayfish Tissue from the Spokane River (ng/g, ww).

Station/Tissue	Sample ID	Size	Mean Length (mm)	Lip	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl	9-Cl	10-Cl	Total PCB
Whole Body Suckers*															
STATELINE-F	4324442	Lg	513	4.5%	<0.02	<0.02	0.67	20.7	43.2	39.7	30.8J	5.78J	0.49	0.12	141.5 J
	4324443	Sm	445	3.4%	<0.02	<0.02	0.08	3.77	14.6	20.1J	16.8	3.02	0.40	0.10	59.0 J
mean=															100.2
PLANTE-F	4324440	Lg	479	4.6%	<0.02	0.03	2.26J	30.2	52.4	25.0	25.9J	3.98	0.28	0.05	140.2 J
	4324441	Sm	453	3.3%	<0.02	0.02	0.76	9.71	19.0	12.7J	8.16	2.87J	0.24	0.04	53.5 J
mean=															96.9
NINEMILE-F	4324447/8†	Lg	431	2.6%	<0.02	0.03	0.56J	3.33J	9.22J	11.0J	4.91J	1.27	0.21 J	0.05	30.6 J
	4324450	Sm	355	4.8%	<0.02	0.06	1.01J	3.86	8.77	9.66	3.49	0.79	0.16	<0.04	27.8 J
mean=															29.2
LONGLOW-F	4324444	Lg	463	7.7%	<0.02	0.06	3.41J	43.4	59.7J	53.9J	25.5	8.17J	1.11	0.11	195.4 J
	4324446	Sm	433	9.1%	<0.02	0.06	4.08J	54.7	74.4J	78.0J	32.0	8.59	1.05	0.18	253.1 J
mean=															224.2
Sucker Gut Contents															
PLANTE-F	4324445	--	485	na	<0.02	0.03	1.38	27.6	44.2	26.8J	14.1	3.40	0.28	0.04	117.8 J
NINEMILE-F	4324449	--	396	na	<0.02	0.02	0.03	0.29	1.13	1.48	0.28	0.05	0.02	<0.04	3.3
Crayfish Tail Muscle															
Upriver Dam	4208148	--	40	na	<0.006	0.02	0.01	0.03	0.036	0.05	0.54	0.18J	0.01	<0.01	0.87 J

*Largescale suckers except bridgelip suckers at NINEMILE-F.

†Mean of replicate analysis.

Detected values are in green highlight.

U: The analyte was not detected at or above the reported result.

J: The analyte was positively identified. The associated numerical value is an estimate.

Largescale suckers from Stateline and Plante Ferry had similar PCB concentrations. Composites of large fish had three times the PCB level of the smaller fish composites at both sites even though average lengths were not substantially different (513 vs. 445 mm at Stateline; 480 vs. 453 mm at Plante Ferry). The higher PCB concentrations in the large fish samples from these sites may be due to the 50% higher lipid content, yet even on a lipid-normalized basis, growth dilution does not appear to be a controlling factor in PCB concentrations.

The Lake Spokane largescale suckers had the highest PCB levels. Size disparity was similar (463 vs. 433 mm), and the sample of smaller fish had 30% higher PCB levels, but here again, the difference is not necessarily due to growth dilution since the sample composed of smaller fish had a 20% higher lipid content.

Bridgelip suckers from Ninemile had much lower PCB concentrations than suckers at other locations, possibly due to species difference or the smaller size of fish at Ninemile (large and small composites averaged 431 and 355 mm, respectively). However, PCB contamination of food items also appears to be a major factor since differences in PCB concentrations in whole fish from Plante Ferry and Ninemile reflect differences in PCB levels in gut contents.

Both rainbow trout and suckers appear to show drastic reductions in PCB concentrations compared to previous sampling. PCBs in rainbow trout fillet from Plante Ferry and Ninemile, when compared on a lipid-normalized basis to reduce covariability, have decreased an order of magnitude from 1999. Largescale suckers analyzed in 2003-2004 have approximately one-fifth the PCB concentrations compared to the previous sampling at Plante Ferry (1996) and lower Lake Spokane (2001). Bridgelip suckers collected from Ninemile in 2004 had much lower total PCB concentrations than the previous [largescale] sucker sampling at this location (880 ng/g lipid in 2004 vs. 31,000 ng/g lipid in 1999).

PCB concentrations in largescale suckers from Plante Ferry and lower Lake Spokane appear to be similar to “boundary conditions” at Stateline when compared on a lipid-normalized basis. This may suggest, generally, that PCB concentrations in certain Washington reaches of the Spokane River are in essence equilibrating to general conditions upstream in Idaho. A recent study of PCBs in Lake Coeur D’Alene fish (SAIC, 2003b) found a total PCB concentration of 1,580 ng/g lipid in whole largescale sucker, similar to the levels in Stateline suckers (2,440 ng/g lipid) as well as other locations analyzed during the present survey (2,340 ng/g lipid at Plante Ferry and 2,660 ng/g lipid at lower Lake Spokane).

An industrial or commercial legacy of PCB contamination is evident in the northern portion of Lake Coeur D’Alene. The SAIC study collected suckers (combined long-nose and large-scale) specifically around the area known as Blackwell Island, just outside the City of Coeur D’Alene. This location is the start of the Spokane River and has a long industrial history. The whole body sucker composites (combined long-nose and large-scale) ranged from 158 to 443 ug/Kg total PCBs. Large-scale sucker fillets collected more broadly from the north quadrant of the lake ranged from 52 to 124 ug/Kg. Much lower levels of 9 to 15 ug/Kg were found in kokanee and largemouth bass fillets more widely composited from the north quadrant of the lake.

Crayfish from the Upriver Dam fine-grained sediment site showed low levels of PCBs in tail muscle (0.87 ng/g total PCB). Previous analyses of muscle tissue from Spokane River crayfish also found mostly undetectable or low (≤ 7 ng/g total PCB) concentrations, indicating crayfish muscle is a poor sentinel of PCB contamination. Whole crayfish have not been analyzed and could have higher PCB concentrations due to gut contents or accumulation in hepatopancreas or other organs.

2005

Table 34 summarizes the data obtained on PCB levels in Spokane River fish during 2005, (Serdar and Johnson, 2006). Mean concentrations of total PCBs (sum of detected Aroclor-equivalents) ranged from 37-234 ug/Kg in sport fish fillets and 56-1,823 ug/Kg in whole largescale suckers.

Table 34. Summary of PCB Concentrations Measured in Spokane River Fish Collected in 2005.

Reach	Species	N* =	Total PCBs (ng/g, wet weight)	
			Mean	Range
Fillet Samples				
Plante Ferry	Rainbow Trout	3	55	48 - 68
Mission Park	Rainbow Trout	3	153	118 - 220
	Mountain Whitefish	3	234	203 - 280
Ninemile	Rainbow Trout	3	73	46 - 94
	Mountain Whitefish	3	139	86 - 172
Upper Lake Spokane	Mountain Whitefish	3	43	36 - 55
	Brown Trout	1	130	- -
	Smallmouth Bass	1	37	- -
Lower Lake Spokane	Mountain Whitefish	6	76	<9.6 - 190
	Smallmouth Bass	3	67	49 - 82
Whole Body Samples				
Stateline	Largescale Sucker	3	56	16 - 77
Plante Ferry	Largescale Sucker	3	122	91 - 180
Mission Park	Largescale Sucker	3	1,823	1,100 - 3,000
Ninemile	Bridgelip Sucker	3	69	52 - 94
Upper Lake Spokane	Largescale Sucker	3	327	160 - 510
Lower Lake Spokane	Largescale Sucker	3	254	109 - 396

*Composites of 4-5 individual fish each, except lower Lake Spokane mountain whitefish were analyzed individually.

In both types of samples, concentrations gradually increased between the Stateline and Mission Park reaches, then decreased from Mission Park down into lower Lake Spokane. The concentrations in Lake Spokane were higher than in the upper part of the river at Stateline and Plante Ferry.

Fish tissue studies often differ in sample size, use of composites vs. individual fish samples, and in other ways and are not appropriate for statistical testing for long-term trends. Therefore a qualitative, weight-of-evidence approach was taken for identifying long-term changes in PCB levels, coupled with a statistical test for significant differences for the limited instances where comparable data exist.

The data were examined to determine if it would be appropriate to normalize to the lipid content of the samples, since concentrations of PCBs and other organochlorines sometimes vary directly with lipid content. For the majority of species and locations, there was not a good correlation between total PCBs and percent lipids (Serdar and Johnson, 2006).

Serdar and Johnson (2006) identified seven data sets, by river reach, where the same fish species and tissues were analyzed for two or more time periods and where the sample size and type was sufficient for statistical analysis (Table 35). They found substantial decreases in fish tissue PCB concentrations for the following reaches:

- Plante Ferry
- Mission Park
- Ninemile
- Upper Lake Spokane

Table 35. Significant Changes Identified in Total PCB Concentrations in Spokane River Sportfish Fillets: Results from Analysis of Variance on Comparable Data Sets, 1994-2005.

Reach	Species	Sample Type	Time Period	<i>p</i> value (Probability)	Significant Change? ($p < 0.10$)
Plante Ferry	Rainbow Trout	composites	1994-1996	1.00	No
			1996-2005	0.34	
			1994-2005	0.01	Decrease
Mission Park	Rainbow Trout	composites	1994-2005	0.85	No
	Mountain Whitefish			0.02	Decrease
Ninemile	Rainbow	composites	1994-1996	0.07	Decrease
			1996-2005	1.00	No
		individuals	1994-2005	0.06	
			1996-2005	0.00	Decrease
	Mountain Whitefish	composites	1994-1996	0.01	Increase
			1996-2005	0.01	Decrease
Upper Lake Spokane	Mountain Whitefish	composites	2001-2005	0.05	Decrease

Appendices D and E of Serdar and Johnson (2006) have the total PCB data for all Spokane River fish tissue samples analyzed by Ecology from 1993 to 2005.

Results of this analysis suggest that, at least for these two species, there has been a significant decrease in PCB concentrations between 1994 and 2005. Evidence for a similar decrease in the Mission Park reach was equivocal. The general picture that emerges from the historical data on the Spokane River is one of decreasing PCB concentrations in fish from all areas of the river since 1994, except perhaps Mission Park.

The long-term declines in PCBs noted along the upper Spokane River both statistically and qualitatively are consistent with recent Ecology regulatory and investigatory actions that are yielding reductions in PCBs entering the river from NPDES discharges and remedial actions associated with cleanups at a major industrial facility. Lake Spokane may also be responding to the actions taken in the upper river. The apparent lack of a decline in PCB levels in fish from the Mission Park reach is consistent with stormwater discharge being the largest current source of PCBs to the river.

Table 36 compares the 2005 results with statewide data on PCBs in freshwater fish, based on fillet data reported by Seiders and Kinney (2004) and whole fish data reported by Davis et al. (1994, 1995, 1996, 1998). The fillet samples were primarily collected during 1995-2002; the whole fish samples are from 1992-1995. To avoid biasing the statewide results high, data for Spokane River fish were excluded. The statewide data do not represent “background” sampling from waters generally free of human influences, but are from various waters around the state including lakes, rivers, and streams also impacted by industrial and municipal discharges.

Table 36. Total PCB Concentrations in Spokane River Fish vs. Statewide Data (ug/Kg, wet weight).

Total PCBs	Spokane River 2005		Statewide	
	Fillet N=24	Whole Body N=24	Fillet N=98	Whole Body N=28
Mean	104	442	155	151
Median	78	135	28	87
Minimum	36	16	1.2	7.1
Maximum	280	3,000	1,943	622
90th percentile	213	1,181	297	334

For the most part, PCB concentrations in the 2005 Spokane River fillet samples are in the range of the statewide mean and median for fillets. The whole fish results for Mission Park and Lake Spokane are at or above the upper end of the range of whole fish statewide values.

Ecology recently completed an assessment of PCB levels in fish from background lakes, rivers, and streams throughout Washington (Johnson et al., 2010). Table 37 compares the results with the 2005 Spokane River edible fish tissue data. Whole body samples were not analyzed for the background study.

Statewide data obtained through the background study suggest that Spokane River fish are elevated by about an order of magnitude over other waterbodies with no obvious sources of contamination. It should be recognized, however, that the local background in the Spokane region may differ from these statewide results.

Table 37. Total PCB Concentrations in Spokane River Fish vs. Statewide Freshwater Background (ug/Kg, wet weight; fillet samples).

Total PCBs	Spokane River 2005 N=24	Statewide Background N=52
Mean	104	4.9
Median	78	1.4
Minimum	36	0.04
Maximum	280	88
90 th percentile	213	6.5

Assessment of PCB Sources

The following section contains an assessment of PCB sources to the Spokane River, which include industrial and municipal effluents, stormwater, the Spokane River at the state line with Idaho, and the Little Spokane River. Loads from other sources are considered inconsequential (Ecology, 1995; Golding, 1996, 2001, 2002).

Deep Creek was initially considered for source assessment in the present study, but the lower section of the creek appears to be a hydraulically losing reach, and no water was present. Previous monitoring of Latah Creek detected no PCBs in the sediments (Johnson and Norton, 2001). The potential for other small tributaries to deliver PCBs to the Spokane River was considered low, and they were not sampled.

Other possible secondary sources to consider are groundwater and atmospheric deposition.

Groundwater has previously been monitored at the Kaiser Trentwood facility to assess its potential as a source of PCBs to the Spokane River, but Hart Crowser (1995) concluded that groundwater inflow was not a primary PCB transport pathway to the river from the facility. In addition, Ecology's Toxics Cleanup Program currently is overseeing the cleanup of PCBs at Kaiser Trentwood to ensure groundwater contamination will not impact the river.

Atmospheric deposition of PCBs is known to be pronounced in areas where cold condensation occurs, such as in the mountains of southern British Columbia and Alberta (Blais et al., 1998). This phenomenon holds the potential to deposit measurable quantities of PCBs in the mountains in the eastern portion of the Spokane River basin, eventually delivering PCBs to Lake Coeur D'Alene through the St. Joe, St. Maries, and Coeur D'Alene Rivers and, excluding industrial sources in Idaho, may partially explain higher than expected concentrations of PCBs in fish from Lake Coeur D'Alene. Delivery of PCBs to Washington from this source would be integrated to a single channel: the Spokane River at Stateline.

The Spokane River basin downstream of the Idaho border would not be ideal for atmospheric deposition due to aridity of the region, and PCBs that are deposited in the area would theoretically be integrated into delivery systems already considered, such as the Little Spokane River and urban stormwater. Deposition of PCBs directly to the surface of the Spokane River would be minimal due to its small surface area relative to the basin area. Atmospheric deposition is an un-quantified source of PCBs to the Spokane River.

Loss of PCBs to the atmosphere through volatilization has also not been quantified. PCB budgets for the Great Lakes area have shown atmospheric flux to be an order of magnitude greater than input and output through surface waters, with loss through volatilization approximately five times greater than atmospheric deposition (EPA, 1993).

PCB Loading Calculations

PCB loads calculated for the present 2003-07 study only include surface water inputs and outflow, generally using the following formula:

$$\text{Equation 6. Daily Load (mg/day)} = C_w \times (10^{-9} \text{ mg/pg}) \times Q \times (86,400 \text{ s/day})$$

Where:

- C_w (concentration in whole water) = concentration of PCBs in water (pg/l).
- Q (discharge) = flow of the delivery system being considered (L/sec).

To simplify the data presentation and maintain consistency with applicable criteria, loads are calculated for total PCBs only.

Industrial and Municipal Effluents

Table 38 shows PCB loads in effluents identified as PCB sources in this study. PCB loads from Liberty Lake WWTP, Inland Empire, and the Spokane WWTP were calculated using a combination of results from the present survey and previous sampling (Table 21). For the Liberty Lake and Spokane WWTPs, loads were calculated using the mean total PCB concentrations and instantaneous flows from 2001 and 2003-2004. For Inland Empire, loads were calculated using the mean total PCB concentrations and instantaneous flows from 2001, 2002, and 2003-2004. In samples where no PCBs were detected, reporting limits were used to calculate the average.

PCB loads from Kaiser were based on total PCB concentrations and instantaneous flows from nine samples collected during 2004 and 2005 (Table 20) since these represent the most current data on PCBs in Kaiser effluent.

Table 38. Estimated PCB Loads in Industrial and Municipal Effluents Discharged to the Spokane River.

Facility	RM	Total PCB (pg/l)	Discharge (ML/day)	Total PCB Load (mg/day)
Liberty Lake WWTP	92.7	1,121	2.5	2.9
Kaiser Trentwood	86.0	1,080	60	65
Inland Empire Paper	82.5	2,544	18	45
Spokane WWTP	67.4	1,364	143	194
Total =				307

ML/day = megaliters/day [0.264 MGD (million gallons per day)].

Urban Stormwater Runoff

For the sampling conducted in 2004, PCB loads delivered to the Spokane River through stormwater were calculated using the “Simple Method” model to estimate runoff volume and calculate contaminant loads (www.stormwatercenter.net/).

For 2007, Parsons calculated the loads from sampled and un-sampled drains in the City of Spokane using two different discharge estimates: (1) calculated by the Simple Method to be consistent with the 2004 data, and (2) the reported discharge volumes from the City of Spokane’s CSO Annual Report for fiscal year 2005. Both loading scenario calculations for the un-sampled drains used the average concentration from the sampled drains. Parsons concluded that the actual loading of PCBs to the river from stormwater is likely somewhere between the two estimates.

For the source assessment study, the loads from the stormwater sewer network were calculated as the sum of the load determined by the Simple Method for the sampled storm drains and the load using the 2005 discharge volumes for the un-sampled storm drains. The magnitude of stormwater discharge plays a large role in the loading calculations. Parsons stated that because direct untreated CSO discharges may occur only during large runoff events, the Simple Method was considered an upper bound.

The sum load from the sampled stormwater basins using the Simple Method was 557 mg/day total PCBs, and the un-sampled stormwater basins using the discharge records from the City of Spokane was 133 mg/day total PCBs.

The Simple Method uses the formula:

$$\text{Equation 7} \quad L = 0.226 * R * C * A$$

Where:

- L = Annual load (lbs).
- R = Annual runoff (inches).
- C = Pollutant concentration (mg/L).
- A = Area (acres).
- 0.226 = Unit conversion factor.

Annual runoff and runoff coefficient were previously presented as Equations 4 and 5.

Tables 39 and 40 show the estimated PCB stormwater loads in the sampled and un-sampled stormwater basins (data from Parsons, 2007).

The total stormwater load (691 mg/day) from the City of Spokane is considered to be the sum of the high load scenario for the sampled stormwater outfalls above and below Monroe St. Dam (557 mg/day) Table 39, and the low load scenario (133 mg/day) for the un-sampled stormwater outfalls, Table 40. The locations of the un-sampled stormwater outfalls were assumed to be half above and half below the Monroe St Dam.

Table 39. PCB Load from Sampled Stormwater Basins based on Simple Method Discharges, Parsons (2007).

Location_ID ¹	Average t-PCB (ng/L) ²	Annual t-PCB Load (lb) ³	Daily t-PCB Load (mg/day) ⁴	Annual t-PCB Load/Acre (mg/acre)
<i>Sampled Stormwater Basins (High CSO Load Scenario)</i>				
Above Monroe St Dam				
GREENE	19.5	0.001	1	12.2
MISSION	16.5	0.001	1.2	8.2
RIVERTON	22.3	0.005	6	9.1
SUPERIOR	17.8	0.007	9	11.5
UNION	97	0.013	16	54.8
ERIECSO (CSO 34)	177	0.336	417	78
WASHINGT	4.05	0.003	3.6	2.9
HOWARDBR	8.74	0.001	0.9	6
Below Monroe St Dam				
LINCOLN	4.36	0.001	0.7	3.9
CLARKE	2.56	0.005	6	1.2
(CSO 24A)				
7 TH (CSO 26)	3.38	0.003	4	2.5
COCHRAN	12.9	0.072	90	6.3
HSTREET (CSO 7)	2.49	<0.001	0.4	1.1
HWY291	0.978	0.002	2	0.4
Totals		0.45	557	198

¹ In EIM these Locations IDs have the prefix STMWTR_; and CSO # in parentheses is not part of Location ID.

² Average of all the samples collected in the 2007 Parsons study; the PCB average was updated by Ecology.

³ Calculated using Equation (5).

⁴ Daily PCB load (mg/day) = Annual load (lb/yr)*453000 mg/lb /365.

Rows highlighted in green correspond to CSO basins.

Table 40. PCB Load from Un-Sampled Stormwater Basins based on 2005 City Discharge Data, Parsons (2007).

Location_ID ¹	Average t- PCB (ng/L) ²	Annual t-PCB Load (lb) ³	Daily t-PCB Load (mg/day) [#]	Annual t-PCB Load/Acre (mg/acre)
29 Un-Sampled Stormwater Basins (Low CSO Load Scenario)				
I05 Upper	23	0.014	17.82	8.7
I04	23	0.007	8.57	18.0
I07	23	0.004	5.01	10.1
CSO 33B	23	0.022	27.80	9.2
CSO 06	23	0.012	14.90	11.3
CSO 12	23	0.010	13.02	12.4
I03	23	0.001	0.73	1.9
CSO 23	23	0.005	5.96	13.3
CSO 41	23	0.002	2.37	9.7
CSO 16B	23	0.002	2.41	7.4
CSO 25	23	0.001	1.08	18.7
CSO 33D	23	0.002	2.41	17.9
CSO 14	23	0.002	1.95	10.0
CSO 10	23	0.001	1.79	11.9
CSO 15	23	0.003	3.64	10.8
CSO 42	23	0.000	0.37	22.5
CSO 40	23	0.002	1.92	12.3
CSO 39	23	0.001	1.60	11.4
CSO 33A	23	0.001	1.77	9.7
CSO 38	23	0.002	2.19	11.2
CSO 24B	23	0.003	3.54	18.2
CSO 33C	23	0.001	0.85	19.3
CSO 20	23	0.005	6.65	9.6
CSO 02	23	0.002	1.95	11.1
CSO 19	23	0.001	0.99	10.6
CSO 16A	23	0.001	0.76	10.7
CSO 03C	23	0.000	0.34	12.3
CSO 18	23	0.000	0.22	6.1
CSO 34TOSVI	23	0.000	0.15	10.9
Totals		0.11	133	347

¹ In EIM these Locations IDs have the prefix STMWTR_ ; and CSO # in parentheses is not part of Location ID.

² Average of all the samples collected in the 2007 Parsons study; the PCB average was updated by Ecology.

³ Calculated using Equation (5).

⁴ Daily PCB load (mg/day) = Annual load (lb/yr)*453000 mg/lb /365.

Rows highlighted in green correspond to CSO basins.

Parsons found the largest stormwater PCB loads to the Spokane River originate from the Cochran, CSO 34, Union Street, and I05 Upper stormwater basins under both discharge scenarios.

Instream Loads

Harmonic Mean Flow

The harmonic mean flow is recommended by EPA (1991a) for use in assessing a river's loading capacity for long-term exposure to carcinogens such as PCBs. Harmonic mean is the appropriate measure of central tendency when dealing with rates, in this case rates of flow. The harmonic mean is less than the arithmetic mean and is expressed as $Q_h = n / \sum(1/Q_i)$, where n is the number of recorded flows and $\sum(1/Q_i)$ is the sum of the reciprocals of the flows.

As noted by EPA (1991b), the harmonic mean “provides a more reasonable estimate than the arithmetic mean to represent long-term average river flow. Flood periods in rivers bias the arithmetic mean above the flows typically measured. This overstates available dilution. The calculation of the harmonic mean, however, dampens the effect of peak flows. As a result, bias is reduced. The harmonic mean is also an appropriate conservative estimate of long-term average flow in highly regulated river basins, such as the Columbia. In a regulated river basin, the harmonic mean and the arithmetic average are often much closer numerically.”

PCB Loads in the Spokane River at the Idaho Border

PCB loads at the Idaho border were calculated using the average dissolved total PCB concentration from 2003-2004 Stateline SPMD data and historic harmonic mean flow at USGS Gage 12419500 (Spokane River above Liberty Bridge). Two methods were used to calculate the whole water PCB concentrations: (1) extrapolation using the dissolved fraction estimated from Equation 3 and (2) addition of the solid component measured in Harvard Rd. suspended particulate matter (Table 41). Both methods yield an estimated total PCB load of approximately 480 mg/day. Results using the two methods are nearly identical since the theoretical dissolved fraction (0.92) is similar to the measured dissolved fraction (0.91).

Table 41. PCB Loads in Spokane River at Idaho Border.

Station	RM	Harmonic Mean Flow (L/sec)	Method for Calculating C_w	Component	Mean Total PCB C_w (pg/l)	Total PCB Load (mg/day)
Stateline	96.1	52,151*	Stateline SPMD (C_d) /diss fraction (0.92) from Equation 3	$C_w=$	106	477
Harvard	92.8	52,151*	Stateline SPMD (C_d) + Harvard suspended particulate matter (C_s)	Diss. (C_d)	97	439
				Solid (C_s)	10	43
				Total (C_w)=	107	482

* Flow from USGS Station 12419500: Spokane River above Liberty Br (RM 93.9).

C_w Concentration in whole water.

PCB Loads in the Little Spokane River

PCB loads in the Little Spokane River were calculated using the average Little Spokane SPMD data from 2003-2004 and historic flows at USGS Gage 12431000 (Little Spokane River at Dartford). Equation 3 was used to estimate dissolved and solid-phase fractions based on TSS concentrations in the Little Spokane River.

The estimated average total PCB load in the Little Spokane River is 97 mg/day (Table 42). Approximately 74% of this load is in the dissolved phase, based on estimation using Equation 3 and an average TSS of 5 mg/L.

Table 42. PCB Loads in the Little Spokane River.

Location	RM	Harmonic Mean Flow (L/sec)	Mean Total PCB C_d (pg/l)	Fraction C_d	Mean Total PCB C_w (pg/l)	Total PCB Load (mg/day)
Little Spokane R.	56.3	5,619*	147	0.74	199	96.6

* Flow from USGS Station: 12431000 Little Spokane River @ Dartford.

PCB Loads in the Mainstem Spokane River

PCB loads estimated from the 2003-2004 monitoring are shown in Table 43. Loads were calculated as described previously, i.e., using harmonic mean flows (from Figure 3), mean data collected using SPMDs, and application of Equation 3 to estimate total PCB concentrations from the dissolved fraction.

Table 43. Instream PCB Loads in Spokane River Reaches and the Little Spokane River.

Location	RM	Harmonic Mean Flow (L/sec)	Mean Total PCB C_d (pg/l)	Fraction C_d	Mean Total PCB C_w (pg/l)	Total PCB Load (mg/day)
Stateline	96.1	52,151 ^a	97	0.92	106	477
Upriver Dam	80.3	53,081 ^b	68	0.88	77	354
Upriver Dam (bottom)	80.3	53,081 ^b	138	0.88	157	721
Monroe St.	74.8	82,239 ^c	179	0.90	199	1,413
Ninemile	63.6	82,758 ^d	265	0.85	311	2,281
Lower Lake Spokane	38.4	106,329 ^e	332	0.83	399	3,664
Little Spokane R.	56.3	5,619 ^f	147	0.74	199	97

^a Flow from USGS Station 12419500: Spokane River above Liberty Br. (RM 93.9).

^b Flow from USGS Station 12419500: Spokane River above Liberty Br. (RM 93.9) plus sum of flows from municipal and industrial facilities.

^c Flow from USGS Station 12422500: Spokane River at Spokane (RM 72.9).

^d Sum of Flows from USGS Station 12422500: Spokane River at Spokane (RM 72.9) and Station 12424000 – Latah (Hangman) Creek at Spokane (RM 72.2).

^e Flow from USGS Station 12433000: Spokane River at Lake Spokane (RM 33.8).

^f Flow from USGS Station 12431000: Little Spokane River at Dartford (RM 56.3).

In the mainstem Spokane River, PCB loads spanned an order of magnitude, from 350 mg/day at Upriver Dam to 3,700 mg/day at lower Lake Spokane (Figure 19). Higher PCB concentrations occurred in reaches with higher flows, compounding the increase in estimated loads traveling downstream. One exception to this pattern occurs at Upriver Dam (mid-depth), where all of the PCB loading can be attributed to loads moving downstream from the Idaho border (Stateline). Although PCB loads estimated at the bottom of the water column are twice those in the middle column, the mid-column loads are probably more representative of the actual river conditions whereas the bottom loads are influenced by localized conditions as discussed previously. With successful completion of the Upriver Dam cleanup, lower bottom-water concentrations of PCBs would be expected.

Loads were not calculated for Little Falls reservoir or the Spokane Arm due to the absence of PCB data from these reaches. However, it is reasonable to assume that instream loads at Little Falls are identical to those at Lake Spokane since there are no known additional PCB sources to the Little Falls reservoir, flow contributions or losses to the reservoir are minor, and residence time is short since Little Falls is a run-of-the-river dam.

These conditions are also true for the upstream half of the Spokane Arm which is free-flowing. The assumption of identical loads in the lower half of the Spokane Arm (approximate delineation at Porcupine Bay [RM 13]) is tenuous due to the influence of Lake Roosevelt which backs up the water in this reach during most of the year and has an undetermined effect on PCB concentrations and loads. Limited evidence suggests that Lake Roosevelt itself contributes at most a small portion of the PCBs to the Spokane Arm and more likely has a diluting effect. PCB concentrations in Lake Roosevelt fish tissues have been low compared to fish from the lower reaches of the Spokane River (EVS, 1998; Munn, 2000).

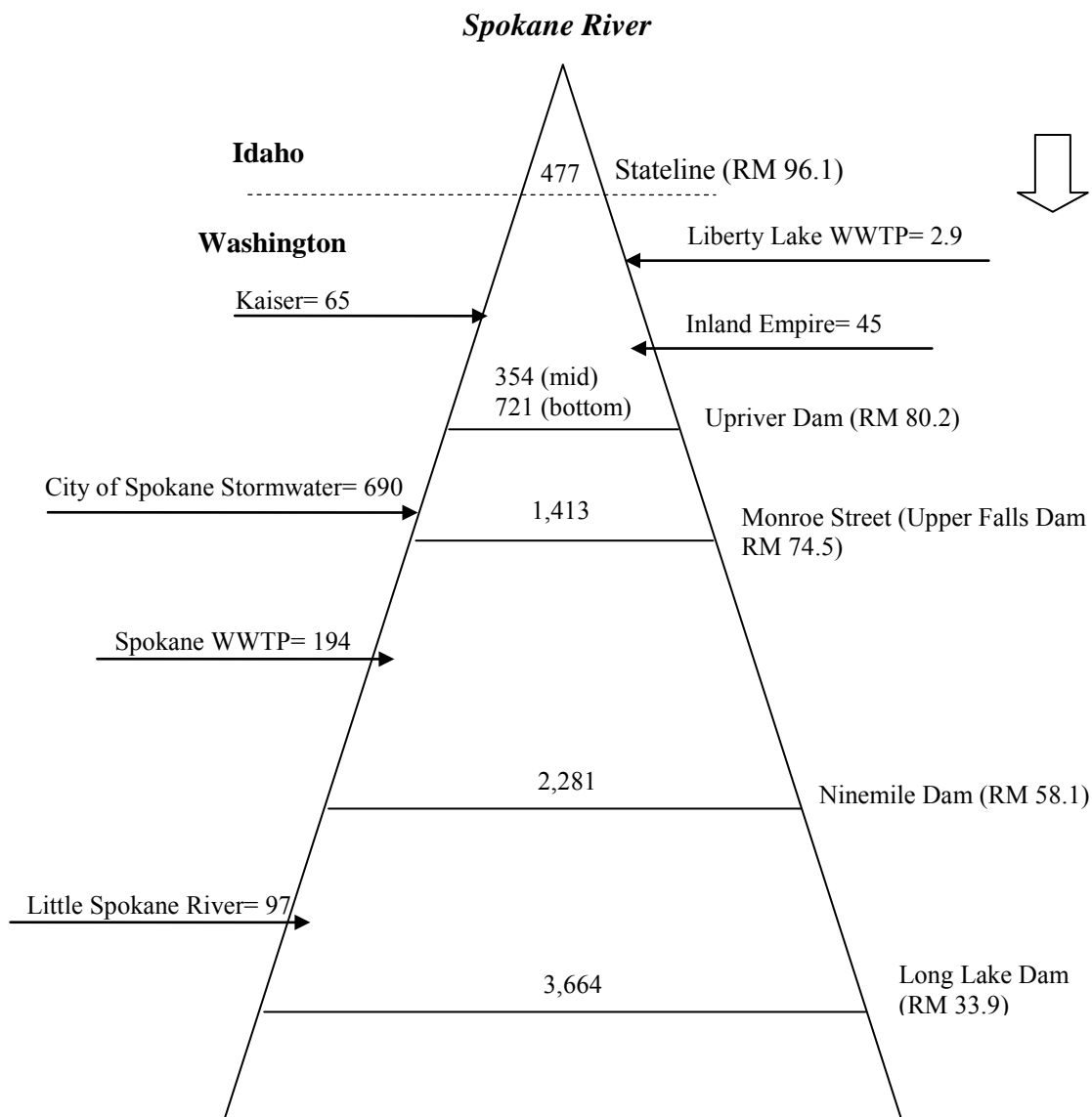


Figure 19. Schematic of PCB Sources and Instream Loads in the Spokane River (total PCB, mg/day).

Load Reductions Needed to Meet Human Health Criteria

Table 44 shows estimates of the reduction in PCB loads that would be needed to meet NTR and Spokane Tribe human health water quality criteria in the mainstem Spokane River and Little Spokane River. The “current” PCB loads were calculated in the preceding section of this report.

Table 44. Estimates of PCB Load Reductions Needed to Meet Human Health Water Quality Criteria in the Spokane River (based on 2003-04 water column data).

Location on Spokane River	Harmonic Mean Flow ^a (l/d)	Current t-PCB Conc. ^a (pg/l)	Current t-PCB Load (mg/day)	Target t-PCB Load (mg/day) at Water Quality Criterion		t-PCB Load Reduction Required to Meet Water Quality Criterion	
				NTR (170 pg/l)	Spokane Tribe (3.37 pg/l)	NTR	Spokane Tribe
Stateline	4.51E+09	106	477	766	15	none required	97%
Upriver Dam	4.59E+09	117	537	780	15		97%
Monroe St.	7.11E+09	199	1,413	1,208	24	15%	98%
Ninemile	7.31E+09	311	2,281	1,243	25	46%	99%
Little Spokane River	4.85E+08	199	97	83	2	15%	98%
Lake Spokane (lower)	9.19E+09	399	3,664	1,562	31	57%	99%
Little Falls	9.19E+09	399	3,664	1,562	31	57%	99%
Spokane Arm	9.19E+09	399	3,664	1,562	31	57%	99%

^a From Table 43

During 2003-04, the Spokane River was meeting the NTR criterion for water (170 pg/l) between Stateline and Upriver Dam but not further downstream. Load reductions of 15-57% would be required to meet this criterion throughout the river, with the largest reductions needed in and below the Ninemile reach. A 15% reduction is called for in the Little Spokane River.

Very large reductions in loading would be required to meet the much more restrictive Spokane Tribe criterion (3.37 pg/l). These range from 97% at Stateline to 99% by Ninemile.

In order for the Spokane River to achieve compliance with human health water quality criteria, reduction of similar magnitude may be needed in loading from municipal and industrial discharges that have been identified as PCB sources. In the Washington reaches of the river, stormwater carries the largest PCB load and is thus the most important source to reduce.

Food Web Bioaccumulation Model

Fish accumulate PCBs through a variety of pathways including bio-concentration (direct uptake of dissolved PCBs in water through the gills and skin), diet, and, in some cases, direct ingestion of sediment. Both the NTR and Spokane Tribe water quality criteria may underestimate the PCB concentrations that will result in a fish because bio-concentration is the only accumulation mechanism considered in the NTR. Previous studies in the Spokane River have found the bio-concentration factor (BCF) of 31,200 L/kg used to derive this criterion to be a poor link between PCB concentrations in water and fish tissue. For instance, Jack et al. (2003) estimated that the BCF explained no more than 23% of the PCB accumulated in Spokane River fish tissue. To accurately relate water concentrations to fish tissue, all pathways must be considered including direct and indirect contributions from sediments.

It is widely recognized that bioaccumulation factors (BAFs) describe a much more meaningful relationship between water and tissue concentrations than BCFs (EPA, 2000b). Like BCFs, BAFs numerically describe the link between water concentrations and accumulation in tissue, but they integrate all exposure pathways (bio-concentration, diet, other sources) and therefore more accurately reflect the water-tissue relationship. Using a simplified computation method, BAFs for the Spokane River were estimated to be in the range of 10^5 - 10^6 L/kg (Jack et al., 2003).

In some cases, sediment may be a more important pathway for PCB exposure in fish, either through consumption of benthic organisms as prey or through direct ingestion of sediments. In instances where sediment exposure is important, the relationship is described as the biota-sediment accumulation factor (BSAF), a tissue concentration divided by a sediment concentration and usually normalized to lipid in tissue and organic carbon in sediment. If a BSAF is much better than a BAF at describing the link between contaminants in the aquatic environment and fish tissue concentrations, then sediment recovery rates (either natural or through cleanup actions) applied to BSAFs may be used to predict contaminant declines in fish tissues. In Lake Spokane, the sediment BSAF calculated from mean sediment and fish tissue concentrations was 10.9 (Jack et al., 2003).

Neither the BAF nor the BSAF by themselves can accurately describe the link between PCBs in the aquatic environment and fish tissue. Because of the interactions among water, sediments, and biota (prey items), it is impossible to account for fish tissue concentrations resulting from exposure to these sources when they are considered independently. Therefore, a mathematical food web bioaccumulation model was used to estimate PCB concentrations in fish tissue and prey items from concentrations in water and sediment.

Water or sediment quality targets based on the model have no regulatory standing without first meeting procedural requirements of site-specific criteria development. However, model development may be a useful exercise to determine if the existing numerical approach is adequate and if site-specific criteria are warranted.

The Model

A food web bioaccumulation model developed by Arnot and Gobas (2004) was selected to predict the PCB concentrations in fish tissues. This model calculates site-specific concentrations of hydrophobic organic chemicals in multiple aquatic ecosystem compartments and is a refinement of a widely used model previously developed by Gobas (1993). The model cannot only be used to predict PCB concentrations in fish tissue, BAFs, and BSAFs using relatively few input parameters, but more importantly, the model can be used to back-calculate PCB concentrations in water and sediment from target PCB concentrations in fish tissue.

A model such as this has potential value for affirming targets for both tribal and non-tribal fish consumers in specific localized areas of the river. In this way, local targets can be set to guide immediate efforts at improving conditions nearer sources, within the realm of practicability.

Details of the Arnot/Gobas model are in Appendix H.

Target Water and Sediment Concentrations

The Spokane Tribe fish tissue criterion for PCBs (0.1 ng/g) was used to calculate target PCB concentrations in water and sediment. The study area was divided into five reaches to establish target PCB loads: Stateline-Upriver Dam, Monroe Street-Ninemile, Lake Spokane, Little Falls, and Spokane Arm. The four reaches upstream of Lake Spokane were collapsed into two – Stateline-Upriver Dam and Monroe Street-Ninemile – due to the lack of input parameters for individual reaches. The Monroe Street-Ninemile reach includes the section from Upriver Dam to Monroe Street dam. Some of the input parameters for Little Falls and Spokane Arm were out-of-date; Lake Spokane input parameters were used for these reaches with the exception of sediment TOC data which were collected at all locations for the present study. Table H-1 shows input parameters used in the model.

Dissolved water and sediment total PCB concentrations predicted to yield the Spokane Tribe criterion of 0.1 ng/g for total PCB in rainbow trout and sucker fillet are shown in Figures 20 and 21. Results show that PCB concentrations in water and sediment one to four orders of magnitude lower than present would be required to achieve the Spokane Tribe fish tissue criterion. The model illustrates the influence of PCBs in sediments on fish tissue, either through the food web or through direct ingestion, and offers a striking contrast to the simple BCF model which ignores PCBs in sediments and diet. When sediment PCB concentrations are set to zero, effectively reducing the food web model to the BCF model, rainbow trout fillet is predicted to have 0.1 ng/g total PCB at whole-water concentrations similar to the BCF model (3.37 pg/l).

Selection of water concentration targets for PCBs is subjective because it depends on sediment PCB concentrations, and conversely, target levels of PCBs in sediments depend on water PCB concentrations. In essence, both water and sediment critical values for PCBs are “moving targets” at an established tissue concentration. This is further complicated by differences in the two fish species being considered at each reach. As a practical matter, the recommended approach to establish target values is to select water and sediment concentrations where lines for rainbow trout and suckers intersect on each of the water-sediment plots in Figures 20 and 21.

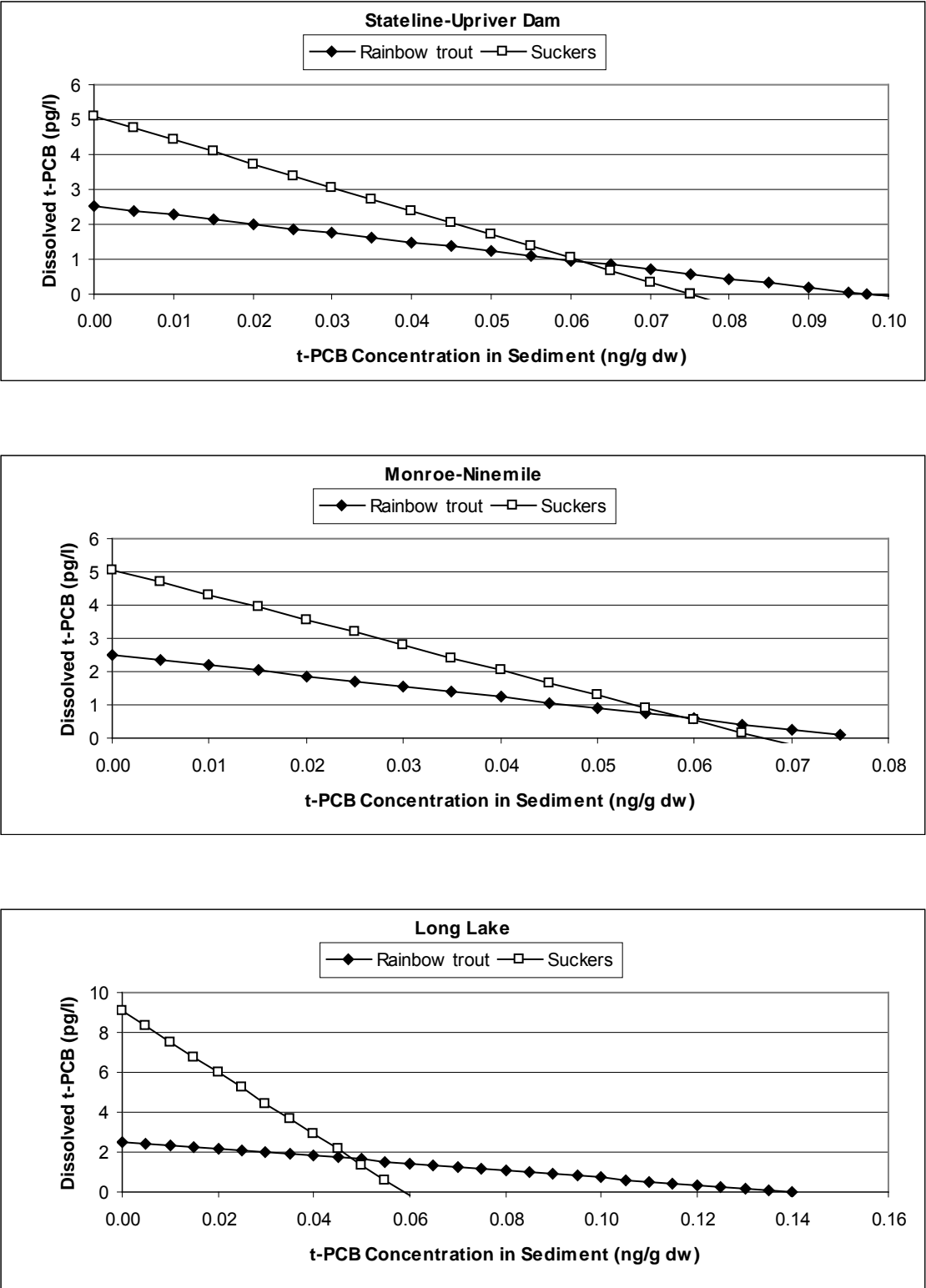


Figure 20. Dissolved Water and Sediment Total PCB Concentrations Predicted to Yield 0.1 ng/g in Rainbow Trout and Sucker Fillet (Stateline to Lake Spokane).

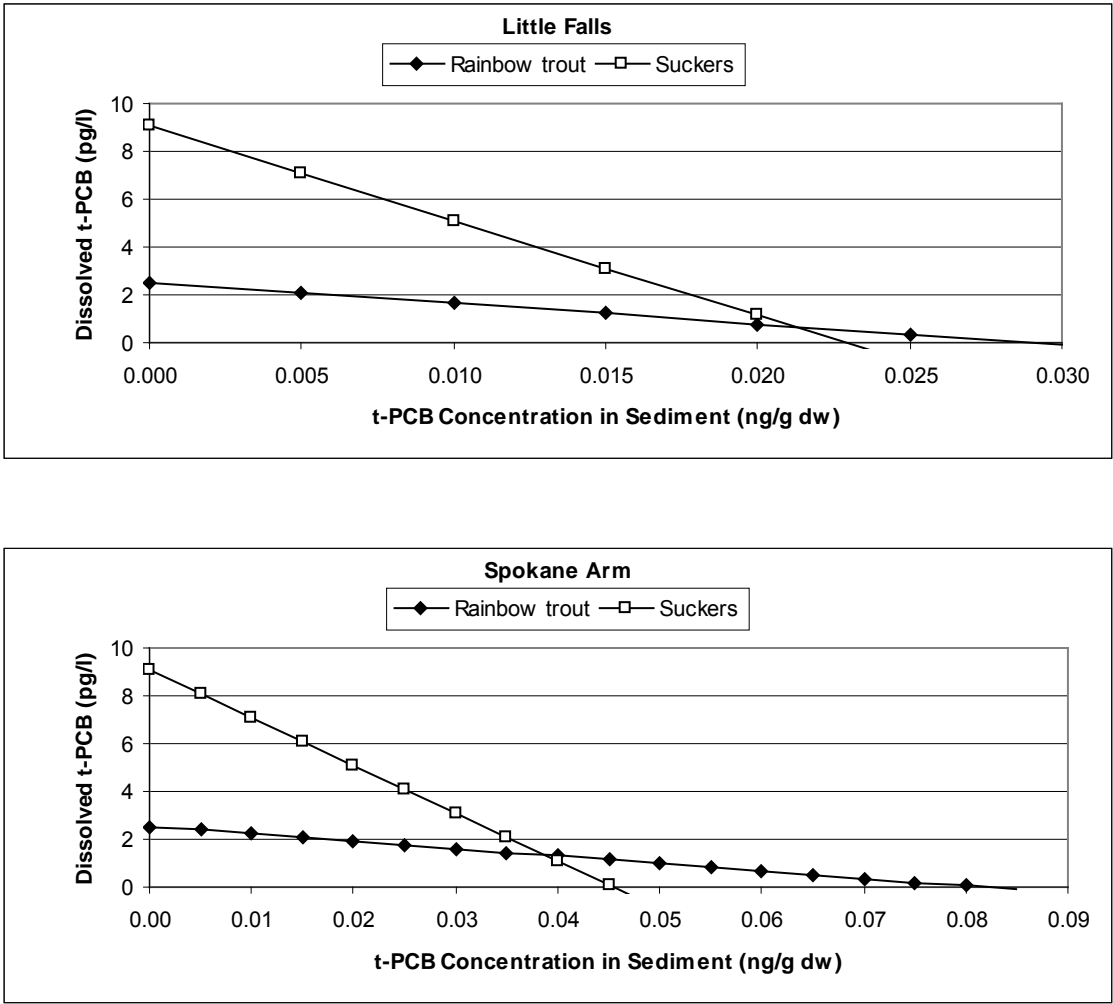


Figure 21. Dissolved Water and Sediment Total PCB Concentrations Predicted to Yield 0.1 ng/g in Rainbow Trout and Sucker Fillet (Little Falls and Spokane Arm).

By using the intersection of two disparate species, the resulting targets will likely be protective of other species that might be consumed. The target water and sediment values may then be computed by setting the equations for each line equal to one another ($[m \times C_s + b]_{\text{Rainbow}} = [m \times C_s + b]_{\text{Sucker}}$) and solving first for sediment concentration (C_s) and then for water concentrations ($C_d = m \times C_s + b$). This approach effectively halves the number of target values required.

Table 45 shows water and sediment targets for PCBs in the Spokane River, calculated using the food web bioaccumulation model. The targets for water are two to five times lower than those established using the Spokane Tribe water criterion.

Here again, the reductions needed in PCB concentrations and loads to meet the model-based targets would be very large. All discharges would require PCB load reductions of $\geq 99\%$. In addition, concurrent reductions of $\geq 99\%$ are indicated for sediment PCB concentrations.

Table 45. Target Sediment and Water Total PCB Concentrations Needed to Yield the Spokane Tribe Fish Tissue Criterion (0.1 ng/g) in the Spokane River, Based on the Arnot-Gobas Food web Bioaccumulation Model.

Reach	Target Tissue Total PCB Conc. (ng/g)	Target Sediment Total PCB Conc. (ng/g dw)	Target Dissolved Water Total PCB Conc. (pg/l)	Dissolved PCB Fraction	Target Whole Water Total PCB Conc. (pg/l)	Target Total PCB Load (mg/day)
Stateline-Upriver Dam	0.1	0.06	0.9	0.90	1.0	4.5
Monroe-Ninemile	0.1	0.06	0.6	0.88	0.7	4.9
Lake Spokane	0.1	0.05	1.7	0.83	2.0	18.7
Little Falls	0.1	0.02	0.7	0.83	0.8	7.7
Spokane Arm	0.1	0.04	1.3	0.83	1.6	14.3

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Conclusions

The overall goal of the Spokane River PCB Source Assessment was to gather representative data to quantify PCB contamination in Washington reaches of the Spokane River. Data were collected in a series of studies conducted between 2003 and 2007. The information collected is being used to (1) identify necessary reductions in PCB sources to meet applicable water quality criteria and (2) develop a strategy for reducing sources to the river.

Specific components of the study included:

- Obtain representative data on PCB concentrations and ancillary parameters in the Spokane River water column, NPDES- permitted discharges, bottom sediments, and fish tissue.
- Assess trends and recovery rates for PCBs in Spokane River sediments.
- Determine the Spokane River's loading capacity for PCBs.
- Evaluate a food web bioaccumulation model to predict the PCB concentrations in Spokane River fish.

Results of sampling during 2003 and 2004 indicate that average PCB concentrations in river water increase with successive reaches from the Idaho border (106 pg/l) to lower Lake Spokane (399 pg/l), with a corresponding eight-fold increase in loads (477-3,664 mg/day). Overall, PCB loading to Washington reaches of the river can be divided into the following source categories: City of Spokane stormwater (44%), municipal and industrial discharges (20%), and Little Spokane River (6%). In addition, PCB loading from Idaho at the state line represented 30% of the overall loading.

Current PCB concentrations in fish tissue are lower than they have been historically. This may be due in part to natural attenuation and significant reductions in point-source PCB contributions over the past 10 to 15 years. The lack of decline in PCB levels in fish from the Mission Park reach of the river supports the conclusion about the importance of stormwater as a PCB source. A food web bioaccumulation model was used to predict PCB concentrations in fish tissue from PCB levels in water and sediments. This model indicates that significant reductions in sediment PCB concentrations would be required to reduce fish tissue to a Spokane Tribe target concentrations at their reservation.

Analysis of sediment cores suggests that PCB concentrations at the sediment surface will decrease by one-half approximately every ten years in upper Lake Spokane, although patterns of material deposition upstream of Lake Spokane require further evaluation. Lower Lake Spokane may be the ultimate sink for fine sediments. In lower Lake Spokane, PCBs have decreased by one-half over two decades after steep declines during the 1960s to mid-1980s.

A load-reduction scenario exercise was developed to show the reductions in water PCB concentrations that would be required to meet the Spokane Tribe's target criterion of 3.37 pg/l at the point where the river runs through the Spokane Tribe's reservation. The scenario requires a 95% PCB load reduction in the Spokane River at the Idaho border. Industrial and municipal discharges between the Idaho border and Lake Spokane require PCB load reductions greater than

99%. Stormwater from the City of Spokane also requires a load reduction of >99%. A 97% PCB load reduction is required in the Little Spokane River.

The food web bioaccumulation model is a useful tool to back-calculate water and sediment concentrations that will result in a target fish tissue PCB concentration. This model was used to develop alternative water and sediment quality goals. The model predicts target PCB concentrations in water and sediment after a target PCB concentration in fish tissue has been established, which in this exercise was the Spokane Tribe PCB tissue criterion of 0.1 ng/g. Based on model-derived targets, all discharges would require PCB load reductions of $\geq 99\%$ to meet target loads.

According to the food web model, water reductions of PCBs may not be enough to achieve the tribal goal. Large PCB reductions in sediments would also be required to meet a fish tissue target of 0.1 ng/g. Even with large reductions in PCBs, it seems unlikely that the Spokane Tribal target of 0.1 ng/g is achievable. This concentration is approximately an order of magnitude lower than the median level (1.4 ng/g) reported in fish tissue from background areas in a 2010 statewide study conducted by Ecology (Johnson et al., 2010). Despite the extremely low tribal criteria, it is clear that further reductions in PCB loading are probably achievable.

Recommendations

Even though significant reductions in PCB levels have been measured in the Spokane River since the 1980s, achieving further reductions in PCBs and other toxic chemicals will be a challenging long-term process. This process requires a comprehensive strategy which uses a combination of activities to reduce toxic chemical loading to the river. To start meeting this challenge, Ecology has drafted a long-term strategy for reducing PCBs and other toxic chemicals in the Spokane River watershed. This plan is called *Reducing Toxics in the Spokane River Watershed* (Ecology, 2009). This strategy can be found at the following link: www.ecy.wa.gov/geographic/spokane/images/clean_up_strategy_toxics_in_srws_82009.pdf.

The Spokane River Toxics Reduction Strategy requires coordination across several Ecology programs, including the Spokane River Urban Waters Program (UWP) which was formed in 2007, to identify and eliminate toxic chemicals at their source. The UWP also works cooperatively with local governments including the City of Spokane and the Spokane Regional Health District.

Under the reduction strategy, PCB source identification and control will largely be carried out by the UWP. The strategy uses a three-pronged approach (prevention, management, and cleanup) to reduce sources. Priority is placed on using a systematic step-wise process to identify potential PCB sources within a conveyance system; then reducing or eliminating sources as they are located. This approach has been used successfully by other cities on the West Coast including San Francisco and Portland.

The conceptual approach to reduce PCBs discharged to the Spokane River should continue to focus on:

5. Identifying PCB sources and reducing or eliminating them from stormwater and wastewater effluents.
6. Examining treatment alternatives for effluent PCB removal.
7. Implementing necessary treatment plant controls.
8. Characterizing PCB transport through groundwater.

In addition, PCB source reduction efforts should be coupled with an ongoing effectiveness monitoring program to evaluate progress in reaching water quality targets. Effectiveness monitoring data will be useful in implementing an adaptive management framework for the watershed.

Future Characterization Activities

Extensive work to characterize PCBs in the Spokane River has been conducted since 1999. Future sampling should consider how the data will be used to either reduce PCB concentrations in fish tissue or to determine how and where PCB reductions may occur. Several activities to consider include the following:

Source Tracing

The UWP and other groups should continue systematic PCB source tracing activities in high-priority conveyance systems (stormwater and municipal/industrial) to identify and eliminate sources where possible. Implementation of an adaptive management approach using narrative limits in NPDES permits should be explored as an option to establish a set of achievable targets for toxic chemical reductions.

Effectiveness Monitoring

Design and implement a coordinated effectiveness monitoring program to track progress in meeting water quality targets. This program should include periodic assessment of PCB concentrations both instream (in water, sediments, and fish tissue) and in discharges to the river.

Food Web Modeling

Refinement of the Arnot-Gobas food web bioaccumulation model is needed to predict conditions necessary to reach PCB target outcomes in priority reaches of the river. Specifically, the model should be examined to determine if modifications to the organism component (both benthic and fish) of the model would yield more accurate outcomes.

The model should be examined to identify critical input parameters that need refinement. Fish diet is a particular area where data refinement is needed. Site-specific field data are preferred to literature values where available.

Output parameters (i.e., fish tissue) should also be analyzed concurrently to assess the model's accuracy. This appears to be particularly important considering the apparent rapid change in fish tissue PCB concentrations.

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Appendices

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Appendix A: Spokane River Basin NPDES Permits

Table A-1. Spokane River Basin NPDES Permits (active during Ecology's 2003-2007 PCB studies).

Facility Name	Permit Type	Permit Number	WRIA
Industrial Facilities			
Newman Lk Flood Control Zone Dist	Minor	WA0045438A	57
B F Goodrich	POTW	ST0008068A	57
Columbia Lighting Inc	POTW	ST0005222B	57
Group Photo	POTW	ST0005378A	57
Johnson Matthey Electronic	POTW	ST0005350B	57
Novation Inc	POTW	ST0005355B	57
Inland Empire Paper Co	Major	WA0000825B	57
Kaiser Trentwood	Major	WA0000892B	57
Dawn Mining Company	State	ST0005230C	54
Avista Corp Headquarters	Minor	WA0045195B	57
Johnson Matthey (Cheney)	POTW	ST0008055A	56
Key Tronic Corp (Spokane)	POTW	ST0005284B	57
Olympic Foods	POTW	ST0008051A	57
Spokane Co Util. (Mica Landfill)	POTW	ST0005356B	56
Wilcox Farms Inc. (Milk Plant)	POTW	ST0005399A	56
Municipal Facilities			
Badger Lake Estates	State	ST0008057B	56
Clayton Sewer District	State	ST0005392A	55
Freeman School District #358	Minor	WA0045403A	56
Liberty School District #362	State	ST0005397A	56
Mullen Hill Terrace Properties	State	ST0008041A	57
Snowblaze Condominiums	State	ST0008039A	57
Spokane Co Util. (Hangman Hills)	State	ST0008045A	56
Upper Columbia Academy	State	ST0008034A	56
Deer Park WWTP	State	ST0008016B	55
Diamond Lake WWTP	State	ST0008029C	55
Medical Lake RWTP	Minor	WA0021148A	54
Liberty Lake Sewer Dist #1	Minor	WA0045144B	57
Spokane AWWTP	Major	WA0024473A	54
Cheney WWTP	Minor	WA0020842B	56
Tekoa WWTP	Minor	WA0023141B	56
Fairfield Town of WWTP	Minor	WA0045489B	56
Rockford Town of WWTP	Minor	WA0044831B	56
Spangle Town of WWTP	Minor	WA0045471A	56

WRIA: Water Resource Inventory Area.

POTW: Publicly-Owned Treatment Works.

WWTP: Wastewater Treatment Plant.

RWTP: Rural Wastewater Treatment Plant.

AWWTP: Advanced Wastewater Treatment Plant.

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Appendix B: Sampling Locations for Spokane River PCB Source Assessment Study

Table B-1. Sampling Locations.

Station ID ¹	Sampling Dates	Sample Type	Location Description	RM	Latitude North		Longitude West
Stateline	10/1-29/2003	SPMD	Just downstream of the I-90 bridge at the Idaho state line	96.1	47° 41' 52 "		117° 2 ' 29 "
	1/28-2/24/2004			"	" " " " "		" " " " "
	4/14-5/12/2004			"	" " " " "		" " " " "
STATELINE-F	7/14/2004	Fish	Idaho state line boundary to first downstream riffle (coordinates at midpont)	96.0	47° 41' 54 "		117° 2 ' 33 "
Harvard	10/20-22/2003	SPM/Water	Near right bank below Harvard Road Bridge	92.8	47° 41' 2 "		117° 6 ' 34 "
LIBLAKE	10/21/2003	Effluent	Liberty Lake Wastewater Treatment Plant effluent*	92.3	47° 40' 40 "		117° 6 ' 44 "
KaiserEff	10/21-22/2003	Effluent	Kaiser effluent before discharge to river	86.0	47° 41' 5 "		117° 13 ' 16 "
	2/2-3/2004			"	" " " " "		" " " " "
	4/26-27/2004			"	" " " " "		" " " " "
KaiserFilt	10/21/2003	Effluent	Kaiser at Filter Outlet	86.0	47° 41' 6 "		117° 13 ' 17 "
	2/2/2004			"	" " " " "		" " " " "
	4/26/2004			"	" " " " "		" " " " "
KaiserLag	10/21/2003	Effluent	Kaiser Lagoon	86.0	47° 41' 6 "		117° 13 ' 16 "
	2/2/2004			"	" " " " "		" " " " "
	4/26/2004			"	" " " " "		" " " " "
PLANTE-F	9/15/2003	Fish	1/8 mi. upstream of RR bridge to riffle at lava boulders below park (coordinates at midpoint)	85.0	47° 41' 41 "		117° 14 ' 18 "
PLANTEFRY	10/28-30/2003	SPM/Water	Off right bank at Plante Ferry Park	84.8	47° 41' 52 "		117° 14 ' 41 "
Inland Emp	10/21/2003	Effluent	Inland Empire effluent*	82.6	47° 41' 13 "		117° 17 ' 2.8 "
	2/2-3/2004			"	" " " " "		" " " " "
	4/26/2004			"	" " " " "		" " " " "
Upriver Dam	10/1-29/2003	SPMD	1/8 mi. upstream of Upriver Dam, off right bank	80.3	47° 41' 13 "		117° 19 ' 29 "
	1/28-2/25/2004			"	" " " " "	"	" " " " "
	4/14-5/12/2004			"	" " " " "	"	" " " " "
	5/13/2004	Crayfish		"	" " " " "	"	" " " " "

Table B-1 (Cont'd). Sampling Locations.

Station ID ¹	Sampling Dates	Sample Type	Location Description	RM	Latitude North						Longitude West				
UPRIVER BOT	10/1-29/2003	SPMD	Above Upriver Dam, off right bank, 2 feet from bottom of riverbed	80.3	47°	41'	13	"			117°	19	'	29	"
	1/28-2/25/2004			"	"	"	"	"	"	"	"	"	"	"	"
	4/14-5/12/2004			"	"	"	"	"	"	"	"	"	"	"	"
STMMISSBR	6/10/2004	Stormwater	Stormwater pipe near intersection of Mission and Perry on right bank	76.5	47°	40'	20	"			117°	23	'	20	"
STMSUPOUT	6/10/2004	Stormwater	Stormwater pipe at Superior Street near Cataldo on right bank	75.7	47°	39'	36	"			117°	23	'	32	"
CS034	6/10/2004	CSO	Combined sewer overflow (CSO) outfall at Erie Street	75.8	47°	39'	41	"			117°	23	'	30	"
MonroeSed	4/14/2004	Sediment	Approximately 60 feet off left bank at first bend upstream of Monroe Street Dam	74.9	47°	39'	52	"			117°	24	'	22	"
Monroe St	10/2-29/2003	SPMD	Upstream of Monroe Street Dam	74.8	47°	39'	48	"			117°	24	'	31	"
	1/28-2/25/2004			"	"	"	"	"	"	"	"	"	"	"	"
	4/14-5/12/2004			"	"	"	"	"	"	"	"	"	"	"	"
STMWASHBR	6/10/2004	Stormwater	Stormwater pipe at west side of Washington Street Bridge on right bank	74.3	47°	39'	51	"			117°	25	'	0.8	"
SPOKWWTP	10/21/2003	Effluent	Spokane Wastewater Treatment Plant effluent*	67.4	47°	41'	51	"			117°	28	'	32	"
	2/2/2004			"	"	"	"	"	"	"	"	"	"	"	"
	4/26/2004			"	"	"	"	"	"	"	"	"	"	"	"
Ninemile1	10/1-29/2003	SPMD	Ninemile reservoir above Plese Flats boat launch	63.6	47°	43'	15	"			117°	30	'	29	"
	1/28-2/24/2004			"	"	"	"	"	"	"	"	"	"	"	"
NINEM SPM	11/3-5/2003	SPM/Water	Off of right bank at Plese Flats, Riverside State Park	63.2	47°	43'	35	"			117°	30	'	43	"
Ninemile2	4/14-5/12/2004	SPMD	Ninemile Pool, downstream of boat launch at Plese Flats	62.4	47°	44'	9	"			117°	30	'	40	"
NINEMILE-F	9/16/2003	Fish Gut Contents	Ninemile reservoir near Seven Mile Bridge	61.7	47°	44'	35	"			117°	31	'	14	"
	7/13/2004	Fish		"	"	"	"	"	"	"	"	"	"	"	"
Spokane-F	9/16/2003	Fish		"	"	"	"	"	"	"	"	"	"	"	"
LongLkUp	5/11/2004	Sediment	Upper Long Lake (Lake Spokane)	54.3	47°	47'	38	"			117°	34	'	11	"

Table B-1 (Cont'd). Sampling Locations.

Station ID ¹	Sampling Dates	Sample Type	Location Description	RM	Latitude North		Longitude West
LONGUP2	6/9/2004	Sediment Core	Upper Long Lake (Lake Spokane)	49.2	47° 50' 6 "		117° 39 ' 3 "
LongLkMid	11/4/2003	Sediment	Middle Long Lake (Lake Spokane)	44.3	47° 53' 10 "		117° 41 ' 28 "
Tum Tum	1/29-2/24/2004	SPMD	Long Lake right bank near Tum Tum	44.2	47° 53' 10 "		117° 41 ' 38 "
Littlefls	11/4/2003	Sediment	Spokane River at pool above Little Falls Dam	29.9	47° 50' 10 "		117° 54 ' 38 "
LONGLOW-F	7/13-14/2004	Fish	Lower Long Lake (Lake Spokane) off left bank approx. 1 mi. upstream of DNR launch	39.4	47° 49' 40 "		117° 44 ' 39 "
LongLkLow	10/2-11/4/2003	SPMD	Lower Long Lake (Lake Spokane)	38.4	47° 49' 44 "		117° 46 ' 8.2 "
	4/13-5/11/2004			"	" " " " "	"	" " " " "
	11/4/2003	Sediment		"	" " " " "	"	" " " " "
LONGLOW2	11/4/2003	Sediment Core	Lower Long Lake (Lake Spokane)	36.0	47° 48' 56 "		117° 48 ' 25 "
SPOK-1	11/6/2003	Sediment	Porcupine Bay - NE of boat launch (upstream)	12.6	47° 53' 3 "		118° 8 ' 59 "
LitlSpokSed	12/10/2003	Sediment	Little Spokane River approximately 1 mi. above SR291 bridge ²	2.3	47° 46' 45 "		117° 31 ' 0.9 "
LitlSpokBr	1/29-2/24/2004	SPMD	Little Spokane River @ SR291 bridge ²	1.1	47° 46' 59 "		117° 31 ' 44 "
	4/14-5/12/2004			"	" " " " "	"	" " " " "
LitlSpokR	10/2-30/2003	SPMD	Little Spokane River left bend in river, adjacent to SR291 ²	0.5	47° 47' 13 "		117° 31 ' 38 "
BUFFALO REF	11/5/2003	Sediment	Buffalo Lake near lake center east of boat launch		48° 3' 56 "		118° 53 ' 20 "

* Location coordinates in North American Datum 1983 (NAD83).

¹ Site identification as used in Ecology's Environmental Information Management System (EIM).

² The mouth of Little Spokane River is at Spokane River mile 56.3.

SPM: suspended particulate matter.

SPMD: semipermeable membrane device.

RM: river mile.

The additional fish collection locations and stormwater stations can be found in Tables 12 and 15 and the original reports, Serdar and Johnson (2006) and Parsons (2007) respectively.

Appendix C: Method Used to Convert PCB Concentrations in SPMD to Water

Background on SPMDs

Semipermeable membrane devices (SPMDs) are used to concentrate dissolved hydrophobic contaminants from the water column. Each SPMD consists of a 91 x 2.5 cm lay-flat, low-density polyethylene tube filled with 1 mL of highly purified triolein. The tube is thin-walled and generally considered nonporous except for small ($\leq 10 \text{ \AA}$) cavities created by the random thermal motions of the polymer chains (see Figure D-1). Freely dissolved hydrophobic contaminants are able to pass through the pores and are sequestered and concentrated in both the triolein and the polyethylene itself.

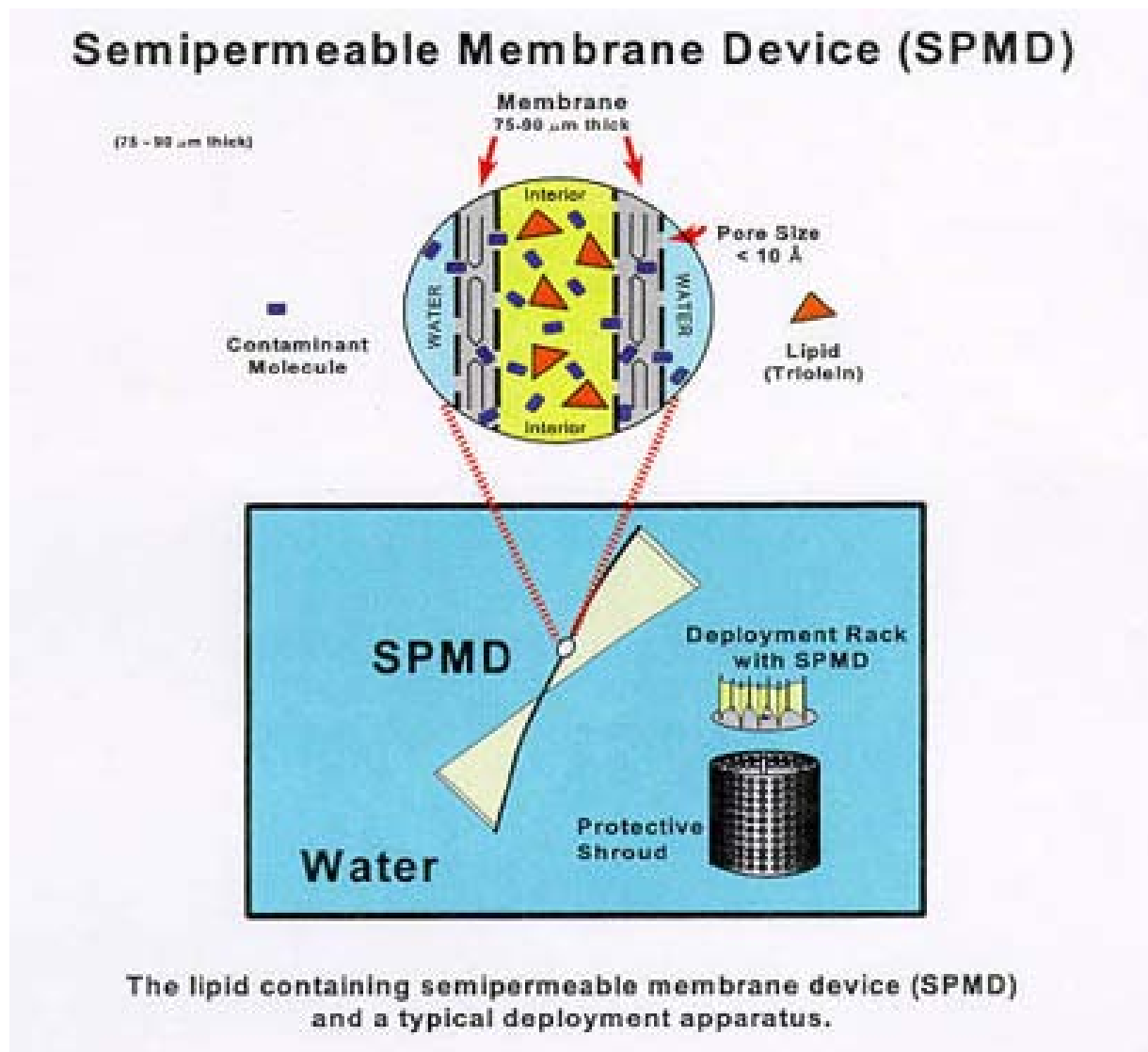


Figure C-1. Illustration of SPMD theory and mechanical design (from Duane Chapman, USGS Columbia Environmental Research Center, www.aux.cerc.cr.usgs.gov/spmd/index.htm)

The SPMDs are mounted on deployment racks (a.k.a. spider carriers) which permit nearly full exposure to surface water. From one to five spider carriers are then mounted inside a protective mesh-skinned stainless steel canister which is placed in the water column for approximately one month.

After removal from the water column, SPMDs are sent to a laboratory for dialytic extraction of the solutes. Prior to dialysis, material coating the SPMD (e.g., periphyton, sediments) is removed, and the membrane is inspected for holes and tears. The dialysate is concentrated to approximately 4 mL in a hexane solvent and stored in an ampule until it is ready for chromatographic or other analysis.

SPMDs are potent samplers of atmospheric organics which present major challenges in avoiding contamination while preparing, deploying, and dialyzing these samplers. To minimize contamination due to air exposure, SPMDs are stored in argon-filled cans following preparation except during their water deployment. Field blank SPMDs are also used to assess the degree of on-site contamination by exposing them to the atmosphere for the same duration as the inevitable exposure of the water sampling SPMDs. Laboratory blank SPMDs are also prepared and analyzed to assess the degree of contamination from the lab environment.

Performance reference compounds (PRCs) are spiked into each membrane prior to deployment to assess sampling rates. The recovery of PRCs, along with other factors such as temperature, water velocity, degree of biofouling, and exposure duration, is used to adjust the site/event-specific sampling rate from sampling rates determined in a laboratory setting. This adjustment factor, commonly referred to as the exposure adjustment factor (EAF), can be applied to the algorithms used to translate chemical concentrations in membrane extract to concentrations in the waterbody sampled.

Methods Used for the 2003-2004 Spokane River PCB Source Assessment Study

Field Blanks

Field (air) blanks were used to adjust SPMD results to account for laboratory and field contamination. The field blank was used for this purpose because it integrates contamination stemming from the field as well as the laboratory. Results for field blanks used during each round of sampling were subtracted (on a per membrane basis) from the sample results.

Exposure Adjustment Factors

PRCs were spiked into all membranes prior to deployment. Selection of PCB congeners for PRCs was based on the congeners found during recent effluent and fish tissue sampling in the Spokane River (Golding, 2002; Jack and Roose, 2002). Four congeners, which were absent or only present in very small amounts in these previous analyses, were used for the spiking solution: PCB-23, 55, 106, and 161. A total of 50 ng of each PRC was spiked into each membrane.

Average PRC recovery was higher than anticipated at 94%. More than a quarter of the PRCs were recovered at $\geq 100\%$. Subsequent consultation with Dr. David Alvarez and Dr. Jim Huckins of the USGS Columbia Environmental Research Center indicated that the fugacity of these congeners is too low to be suitable for calculation of EAFs (PCB-4 and 23 were recommended). Instead, they proposed using laboratory-derived sampling rates to calculate water concentrations.

Calculation of PCB Concentrations in Water

The following equation is the formula, in its simplest form, used to translate chemicals in SPMDs to water column concentrations:

$$C_W = C_{SPMD} / K_{SPMD} (1 - \exp [-k_e t])$$

Where:

C_W = analyte concentration in water

C_{SPMD} = analyte concentration in the SPMD

K_{SPMD} = equilibrium SPMD-water partition coefficient

k_e = first-order loss rate constant

t = time

Derivation of each term is beyond the scope of the present report but can be found at:

wwwaux.cerc.cr.usgs.gov/spmd/SPMD-Tech_Tutorial.htm#MODELING

or in:

Huckins, J.N. Petty, J.D., Priest, H.F., Clark, R.C., Alvarez, D.A., Orazio, C.E., Lebo, J.A., Cranor, W.L., and Johnson, B.T, 2000. A Guide for the Use of Semipermeable Membrane Devices (SPMDs) as Samplers of Waterborne Hydrophobic Organic Contaminants. Report for the American Petroleum Institute (API), Washington, D.C. API Publication No. 4690.

To facilitate translation of SPMD analyte concentrations to water, David Alvarez has developed a spreadsheet which requires relatively few input parameters to make the necessary calculations. Necessary input parameters are temperature, exposure duration, volume and mass of SPMD, total mass of analyte in SPMD, and EAF if PRCs are used to adjust sampling rates. The spreadsheet includes default values for $\log K_{ow}$ and for laboratory sampling rates in cases where EAFs are not used (Table C-1). All calculations are made using the input parameters and the default values in Table C-1 and using the river conditions and exposure periods described earlier in this report. Total analyte mass by PCB homologue group is shown in Table C-2.

Table C-1. Log K_{ow} and Sampling Rates Used to Calculate PCB Concentrations in Water.

Individual PCB Congeners	Log K _{ow}		Laboratory Sampling Rate (L/d)
4	5.1	k,m	12.8
5	5.1	k,m	12.8
6	5.1	g	12.8
7	5.1	k,m	12.8
8	5.1	k,m	12.8
9	5.1	k,m	12.8
10	5.1	k,m	12.8
11	5.1	k,m	12.8
15	5.1	k,m	12.8
16	5.5	k,m	6.7
17	5.5	k,m	6.7
18	5.2	g	9.2
19	5.0	g	5.3
20	5.5	k,m	6.7
22	5.6	g	5.7
24	5.5	k,m	6.7
25	5.7	g	5.7
26	5.7	g	5.7
27	5.5	k,m	6.7
28	5.7	g	8.4
31	5.7	g	7.0
32	5.5	k,m	6.7
33	5.5	k,m	6.7
34	5.5	k,m	6.7
35	5.5	k,m	6.7
37	5.5	k,m	6.7
40	5.7	g	6.6
41	5.7	g	6.2
42	5.8	g	6.2
43	5.8	g	6.2
44	5.8	g	7.5
45	5.5	g	7.9
46	5.5	g	4.4
47	5.8	g	7.5
48	5.8	g	3.5
49	5.8	g	5.3
51	5.6	g	4.8
52	5.8	g	6.2
53	5.6	g	4.8
54	5.9	k,m	5.7

Table C-1 (Cont'd). Log K_{ow} and Sampling Rates Used to Calculate PCB Conc. in Water.

Individual PCB Congeners	Log K _{ow}		Laboratory Sampling Rate (L/d)
55	5.9	k,m	5.7
56	5.9	k,m	5.7
57	5.9	k,m	5.7
58	5.9	k,m	5.7
59	5.9	k,m	5.7
60	5.9	k,m	5.7
63	6.2	g	5.3
64	6.0	g	7.5
66	6.2	g	5.3
67	6.2	g	5.3
69	5.9	k,m	5.7
70	6.2	g	7.0
71	5.9	k,m	5.7
72	5.9	k,m	5.7
74	6.2	g	6.2
75	5.9	k,m	5.7
77	6.2	a, h	2.9
78	6.4	a, h, k	4.4
79	6.4	a, h, k	5.1
81	6.4	g, h	4.3
82	6.2	g	4.4
83	6.3	g	4.8
84	6.0	g	4.4
85	6.3	g	4.8
86	6.4	k,m	4.7
87	6.3	g	5.3
90	6.4	g	6.2
91	6.1	g	4.4
92	6.4	g	5.3
95	6.1	g	6.2
96	6.4	k,m	4.7
97	6.3	g	4.4
99	6.4	g	4.4
101	6.4	g	6.2
102	6.4	k,m	4.7
105	6.6	g	4.0
107	6.7	g	5.3
109	6.4	k,m	4.7
110	6.5	g	5.7
112	6.4	k,m	4.7
113	6.4	k,m	4.7

Table C-1 (Cont'd). Log K_{ow} and Sampling Rates Used to Calculate PCB Conc. in Water.

Individual PCB Congeners	Log K _{ow}		Laboratory Sampling Rate (L/d)
114	6.6	g	4.4
115	6.4	k,m	4.7
117	6.4	k,m	4.7
118	6.7	g	4.8
119	6.6	g	4.4
122	6.4	k,m	4.7
123	6.4	k,m	4.7
126	6.7	a, h, k	2.2
127	6.7	a, h, k	1.6
128	6.7	g	4.4
129	6.7	g	3.5
130	6.8	g	4.0
131	6.8	k,m	4.1
132	6.8	k,m	4.1
133	6.8	k,m	4.1
134	6.6	g	4.8
136	6.2	g	5.3
137	6.8	g	3.5
138	6.8	g	4.8
139	6.8	k,m	4.1
141	6.8	g	4.8
144	6.8	k,m	4.1
146	6.9	g	4.8
147	6.8	k,m	4.1
149	6.7	g	5.7
151	6.6	g	5.3
153	6.9	g	3.2
156	7.2	g	2.6
157	7.2	g	2.6
158	7.0	g	3.5
163	6.8	k,m	4.1
164	6.8	k,m	4.1
166	6.8	k,m	4.1
167	6.8	k,m	4.1
169	7.4	a, h	2.1
170	7.1	k,m	2.6
171	7.1	k,m	2.6
172	7.3	g	1.3
173	7.1	k,m	2.6
174	7.1	g	3.1
175	7.1	k,m	2.6

Table C-1 (Cont'd). Log K_{ow} and Sampling Rates Used to Calculate PCB Conc. in Water.

Individual PCB Congeners	Log K _{ow}		Laboratory Sampling Rate (L/d)
176	6.8	g	2.2
177	7.1	k,m	2.6
178	7.1	g	3.1
179	6.7	g	2.2
180	7.4	g	2.6
183	7.2	g	3.1
185	7.1	k,m	2.6
187	7.2	g	3.5
189	7.1	k,m	2.6
190	7.1	k,m	2.6
191	7.1	k,m	2.6
193	7.1	k,m	2.6
194	7.8	g	1.3
195	7.6	k,m	1.6
196	7.6	k,m	1.6
197	7.6	k,m	1.6
198	7.6	k,m	1.6
199	7.6	g	1.6
200	7.6	k,m	1.6
201	7.3	g	1.6
202	7.6	k,m	1.6
203	7.6	k,m	1.6
205	7.6	k,m	1.6
206	7.7	k,m	1.6
207	7.7	g	1.6
208	7.7	k,m	1.6
Total PCB ^{g, h}	6.4	g, h	4.8

Compounds are listed in general order of their chromatographic elution on a DB-35MS and a DB-5 GC-column for the organochlorine pesticides and PAHs respectively.

The linear model of estimation was used in cases where a compound's log K_{ow}>6.

This calculator applies only to SPMDs which conform to the surface area-to-volume ratio of a standard SPMD.

If multiple log K_{ow} values were found in the literature, a mean value was selected using the t test at 95% Confidence for rejection of outliers.

^a Mackay, D.; Shiu, W-Y; Ma, K-C. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Volume V, Lewis Publishers, Boca Raton, 1997.

^g Meadows, J.C.; Echols, K.R.; Huckins, J.N.; Borsuk, F.A.; Carline, R.F.; Tillit, D.E. Environ. Sci. Technol., 1998, 32, 1847-1852.

^h Rantalainen, A.L.; Cretney, W.; Ikononou, M.G. Chemosphere, 2000, 40, 147-158.

^k Log K_{ow} values estimated from similar congeners.

^m R_s values estimated as the average of known R_s values of similarly substituted congeners

Table C-2. PCB homologue groups in SPMDs (pg per membrane)

Station Name	Sample Number	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl	9-Cl	10-Cl	Total PCBs
October												
STATELINE	474155	42	729	2,117	2,557	7,628	2,173	602	108	0	0	15,957
UPRIVER DAM	474156	74	2,385	4,787	4,196	4,194	970	237	0	0	0	16,843
UPRIVER DAM(REP)	474157	71	2,301	5,208	4,272	4,565	1,324	323	0	0	0	18,063
UPRIVER BOT	474158	35	1,994	6,125	7,974	5,888	1,476	365	35	0	0	23,891
MONROEST	474159	64	4,159	6,224	9,594	9,033	4,940	1,312	128	0	0	35,454
NINEMILE	474160	39	6,847	12,144	10,254	13,492	5,864	1,605	144	0	0	50,389
LONGLOW	474161	80	7,395	14,935	51,689	32,233	10,102	2,747	484	30	0	119,693
LITTLSPOK	474162	0	634	3,605	5,814	5,191	2,321	849	514	69	0	18,998
LITTLSPMS	474163	41	154	1,336	3,217	4,352	1,415	989	450	74	0	12,030
February												
STATELINE	194130	0	24	359	767	1,982	1,007	373	0	0	0	4,511
UPRIVER DAM	194131	7	337	1,126	2,089	2,025	441	1,384	0	0	0	7,409
UPRIVER DAM(REP)	194132	0	125	86	271	338	62	6	0	0	0	888
UPRIVER BOT	194133	2	176	2,087	6,796	3,158	486	69	0	0	0	12,774
MONROEST	194134	0	561	1,903	3,596	2,873	1,552	841	0	0	0	11,326
TUMTUM	194135	4	698	2,317	3,834	2,368	988	895	6	0	0	11,109
LSPOKBR	194136	10	274	2,323	6,929	7,818	2,096	1,146	598	84	0	21,278
LSPOKBRMS	194137	14	83	1,063	4,342	5,711	1,388	639	477	60	0	13,778
April												
STATELINE	208134	0	61	1,564	2,781	8,261	3,737	2,022	88	0	0	18,513
UPRIVER DAM	208135	0	0	411	2,663	2,001	748	350	36	0	0	6,208
UPRIVER BOT(REP)	208137	75	432	5,345	11,499	6,211	1,898	758	48	0	0	26,266
UPRIVER BOT	208136	343	184	4,330	14,517	9,800	2,144	902	0	0	0	32,219
MONROE ST	208138	17	815	4,211	8,830	11,189	4,663	2,299	176	0	0	32,198
NINEMILE2	208139	49	1,202	4,870	9,609	9,742	4,747	2,079	174	0	0	32,470
LONGLKLOW	208133	62	3,086	5,083	15,707	12,072	4,026	1,211	143	0	0	41,389
LITLSPOKBR	208140	0	261	3,560	8,285	9,617	2,779	1,424	720	131	0	26,778
LSPOKBRMS	208141	65	367	3,491	4,126	5,386	1,464	2,071	581	91	70	17,712

REP: replicate.

Appendix D: Ancillary Parameters for Suspended Particulate Matter Sampling

Table D-1. Ancillary Data Taken at Centrifuge Locations During Suspended Particulate Matter Sampling (mg/L).

Station Name	Sample Number	Collection Date	TOC		DOC		TSS	
			inlet	outlet	inlet	outlet	inlet	outlet
Harvard								
	3438100	10/20/03	1.2	---	---	---	2	---
	3438101	10/21/03	1.1	---	---	---	1 U	---
	3438102		1.2	---	---	---	1	---
	3438103		1.1	---	---	---	1	---
	3438104		---	1.2	---	---	---	1 U
	3438105	10/22/03	1.1	---	---	---	1	---
	3438106		1.2	---	---	---	1 U	---
	3438107		---	2.3	---	---	---	1 U
PLANTEFRY								
	3448100	10/28/03	1.1	---	1.1	---	1	---
	3448101	10/29/03	1.1	---	1	---	3	---
	3448102		1.1	---	1	---	1	---
	3448103		---	1.1	---	1 U	---	1 U
	3448104		1.1	---	1	---	2	---
	3448105	10/30/03	---	1	---	1 U	---	1 U
	3448106		1.1	---	1	---	2	---
NINEM SPM								
	3454105	11/3/03	1	---	1 U	---	1	---
	3454106	11/4/03	1 U	---	1 U	---	1	---
	3454107		1 U	---	1 U	---	1	---
	3454108		---	1 U	---	1 U	---	1 U
	3454109		1 U	---	1 U	---	2	---
	3454128	11/5/03	1 U	---	1 U	---	1	---
	3454129		---	1 U	---	1 U	---	1 U

U: Undetected at value shown.

Appendix E: Biological Data for Fish and Crayfish Specimens Used for PCB Analysis

Table E-1. Biological Data for Plante Ferry Rainbow Trout Fillet Specimens.

Fillet Sample No.	Field ID	Date Collected	Total Length (mm)	Fork Length (mm)	Weight (g)	Fillet Weight (g)	Sex	Age (yrs)	Comments on Sex
188308	PF6	9/15/03	404	387	640	206	M	nd	
	PF8		365	350	552	190	M	nd	
	PF11		407	394	714	214	M	4	
	PF14		359	342	454	206	Imm. M?	3	
	PF15		323	308	363	126	M	3	
	PF16		300	284	291	106	M	2	
	PF17		380	364	582	212	M	3	
	PF18		422	401	782	202	M	3	
	PF23		345	328	452	126	Imm. M?	2	
	PF27		321	301	332	136	Imm. M?	2	
		Mean=	363	346	516	172		3	
188309	PF4	9/15/03	385	363	551	196	F	3	eggs visible
	PF5		410	387	670	208	F	4	eggs visible
	PF13		388	369	585	238	F	3	eggs visible
	PF19		412	385	667	210	F	4	eggs visible
	PF20		427	408	760	258	F	3	eggs visible
	PF21		376	356	583	178	F	3	eggs visible
	PF22		387	366	560	178	F	4	eggs visible
	PF24		378	359	517	220	F	3	eggs visible
	PF25		401	387	663	216	F	3	eggs visible
	PF26		345	325	427	202	F	2	eggs visible
		Mean=	391	371	598	210		3	

Imm. = Immature

Table E-2. Biological Data for Plante Ferry Rainbow Trout Gut Content Specimens.

Gut Content Sample No.	Field ID	Date Collected	Total Length (mm)	Fork Length (mm)	Weight (g)	Gut Contents (g)*	Sex	Age (yrs)
188311	PF4	9/15/03	385	363	551		F	3
	PF5		410	387	670	7	F	4
	PF6		404	387	640	1	M	nd
	PF8		365	350	552	15	M	nd
	PF11		407	394	714	1	M	4
	PF13		388	369	585	9	F	3
	PF14		359	342	454	5	Imm. M?	3
	PF15		323	308	363	1	M	3
	PF16		300	284	291	4	M	2
	PF17		380	364	582	3	M	3
	PF18		422	401	782	19	M	3
	PF19		412	385	667	12	F	4
	PF20		427	408	760	11	F	3
	PF21		376	356	583	14	F	3
	PF22		387	366	560	nm	F	4
	PF23		345	328	452	1	Imm. M?	2
	PF24		378	359	517	nm	F	3
	PF25		401	387	663	empty	F	3
	PF26		345	325	427	nm	F	2
	PF27		321	301	332	nm	Imm. M?	2
		Mean=	373	355	546			3

* Total sample weight = 16 g.

Table E-3. Biological Data for Ninemile Rainbow Trout Fillet Specimens.

Fillet Sample No.	Field ID	Date Collected	Total Length (mm)	Fork Length (mm)	Weight (g)	Lipids (%)	Sex	Age (yrs)	Origin
084281	NM1	9/16/03	334	321	413	1.5	Imm. M?	1	hatchery
084282	NM2		357	340	454	2.6	F	2	wild
084283	NM3		320	307	306	1.3	Imm. M?	1	hatchery
084284	NM4		308	290	306	1.9	M	1	wild
084285	NM5		350	332	471	1.1	F	3	wild
084286	NM6		300	282	289	1.0	Imm. M?	1	hatchery
084287	NM7		290	272	290	0.4	Imm. M?	1	hatchery
084288	NM8		333	321	425	1.9	M	1	hatchery
084289	NM9		377	365	483	0.7	F	3	wild
084290	NM10		328	315	380	3.3	M	3	wild
084291	NM11		333	316	376	2.5	F	3	wild
084292	NM12		342	325	421	2.0	Imm. M?	1	hatchery
084293	NM13		296	281	266	1.8	Imm. M?	1	wild
084294	NM14		289	273	257	1.0	M	1	hatchery
084295	NM15		283	273	268	0.6	Imm. M?	1	hatchery
084296	NM16		295	280	251	0.4	Imm. M?	1	hatchery
084298	NM18		296	285	320	0.9	M	1	hatchery
084299	NM19		275	261	227	0.2	Imm. M?	1	hatchery
084301	NM21		297	282	255	1.5	Imm. M?	1	wild
084302	NM22		282	269	250	0.8	Imm. M?	1	hatchery
084303	NM23		362	352	503	0.9	F	2	wild
084304	NM24		265	251	231	0.3	Imm. M?	1	hatchery
084305	NM25		286	270	244	0.5	Imm. M?	1	hatchery
084306	NM26		268	252	201	1.6	M	1	wild
		Mean=	311	296	329	1.3		1	

Table E-4. Biological Data for Ninemile Rainbow Trout Gut Content Specimens.

Gut Content Sample No.	Field ID	Date Collected	Total Length (mm)	Fork Length (mm)	Weight (g)	Gut Contents (g)*	Sex	Age (yrs)
188310	NM3	9/16/03	320	307	306	1	Imm. M?	1
	NM5		350	332	471	2	F	3
	NM6		300	282	289	4	Imm. M?	1
	NM9		377	365	483	1	F	3
	NM11		333	316	376	1	F	3
	NM13		296	281	266	3	Imm. M?	1
	NM14		289	273	257	5	M	1
	NM17		260	245	190	1	Imm. M?	
	NM18		296	285	320	5	Imm. M?	1
	NM19		275	261	227	5	Imm. M?	1
	NM23		362	352	503	2	F	2
	NM25		286	270	244	2	Imm. M?	1
	NM26		268	252	201	1	M	1
		Mean=	309	294	318			2

* Total sample weight = 22 g.

Table E-5. Biological Data for Stateline Largescale Sucker Whole Body Analysis Specimens.

Whole Body Sample No.	Field ID	Date Collected	Total Length (mm)	Weight (g)	Age (yrs)
328442	SL-5	7/14/04	556	1584	13
	SL-6		566	1618	18
	SL-7		483	984	11
	SL-8		521	1168	13
	SL-12		492	1070	8
	SL-15		499	1028	10
	SL-16		476	979	8
		Mean=	513	1204	12
328443	SL-4	9/17/03	460	909	9
	SL-9	7/14/04	459	940	11
	SL-10		457	973	11
	SL-11		427	707	7
	SL-13		433	765	7
	SL-14		471	868	9
	SL-17		408	731	6
		Mean=	445	842	9

Table E-6. Biological Data for Plante Ferry Largescale Sucker Whole Body Analysis Specimens.

Whole Body Sample No.	Field ID	Date Collected	Total Length (mm)	Weight (g)	Age (yrs)
328440	PF-32	9/15/03	463	1093	10
	PF-33		515	1325	8
	PF-38		458	1099	8
	PF-40		485	1117	7
	PF-42		502	1210	7
	PF-43		465	1061	7
	PF-46		440	981	6
	PF-47		501	1250	9
	PF-50		476	1095	9
	PF-51		489	1097	8
		Mean=	479	1133	8
328441	PF-28	9/15/03	475	1094	11
	PF-31		454	1082	8
	PF-35		477	992	7
	PF-36		435	903	5
	PF-41		416	797	6
	PF-48		433	800	7
	PF-49		442	843	9
	PF-52		454	1127	7
	PF-53		460	1043	8
	PF-54		482	963	7
		Mean=	453	964	8

Table E-7. Biological Data for Plante Ferry Largescale Sucker Gut Content Specimens.

Gut Content Sample No.	Field ID	Date Collected	Total Length (mm)	Weight (g)	Gut Contents (g)*	Age (yrs)
328445	PF-29	9/15/03	443	775	5	8
	PF-34		506	1205	17	10
	PF-37		460	893	8	9
	PF-39		424	704	2	6
	PF-44		532	1599	12	10
	PF-45		544	1379	9	8
		Mean=	485	1093		9

* Total sample weight = 53 g.

Table E-8. Biological Data for Ninemile Bridgelip Sucker Whole Body Analysis Specimens.

Whole Body Sample No.	Field ID	Date Collected	Total Length (mm)	Weight (g)	Age (yrs)
328447/8	NM-31	7/13/04	475	980	15
	NM-33		414	820	6
	NM-34		442	693	10
	NM-40		432	881	7
	NM-41		406	673	9
	NM-47		427	616	9
	NM-51		421	826	8
		Mean=	431	784	9
328450	NM-36	7/13/04	358	466	5
	NM-42		356	468	5
	NM-43		351	476	5
	NM-44		358	511	6
	NM-48		355	426	6
	NM-49		357	486	6
	NM-50		351	460	5
		Mean=	355	470	5

Table E-9. Biological Data for Ninemile Bridgelip Sucker Gut Content Specimens.

Gut Content Sample No.	Field ID	Date Collected	Total Length (mm)	Weight (g)	Gut Contents (g)*	Age (yrs)
328449	NM-32	7/13/04	393	695	3	5
	NM-35		401	631	8	5
	NM-37		411	665	6	7
	NM-38		408	732	16	6
	NM-39		408	626	4	6
	NM-45		366	533	6	6
	NM-46		385	536	12	7
		Mean=	396	631		6

* Total sample weight = 55 g.

Table E-10. Biological Data for Lake Spokane Largescale Sucker Whole Body Analysis Specimens.

Whole Body Sample No.	Field ID	Date Collected	Total Length (mm)	Weight (g)	Age (yrs)
328444	LL-2	7/13-14/2004	463	950	10
	LL-7		475	897	10
	LL-14		458	1155	11
	LL-17		445	1003	7
	LL-18		444	897	7
	LL-19		457	934	6
	LL-21		501	1335	9
	LL-23		466	986	5
	LL-24		473	1004	9
	LL-25		450	966	8
		Mean=	463	1013	8
328446	LL-1	7/13-14/2004	440	733	8
	LL-4		425	707	7
	LL-5		439	895	8
	LL-9		416	742	8
	LL-10		433	950	8
	LL-11		442	881	9
	LL-15		439	856	6
	LL-16		458	939	11
	LL-20		415	700	6
	LL-22		425	799	5
		Mean=	433	820	8

Table E-11. Biological Data for Crayfish Tail Muscle Analysis Specimens.

Sample No.	Field ID	Carapace Length (mm)	Date Collected	Weight (g)	Tail Muscle Weight (g)	Sex
208148	1	37	5/12-13/2004	41	5	F
	2	42		53	5	M
	3	39		53	4	M
	4	36		46	4	M

Appendix F: Fish Tissue Preparation, 2003-2005

Whole Body

Suckers for whole body analysis were prepared by removing them from the freezer and allowing them to partially thaw. Plans to composite specimens by sex were abandoned after numerous specimens were opened and gonads were either not found or of indeterminate type. As an alternative, specimens were grouped by length to form a small composite sample and a large composite sample, although size did not vary appreciably among fish. This allowed composites to be formed according to EPA recommendations where the smallest fish in the composite was at least 75% of the length of the largest fish (EPA, 2000a).

Scales and opercula were removed from suckers and mounted or stored for subsequent aging according to Washington Department of Fish and Wildlife (WDFW) protocols. The partially thawed fish were chopped or sawed into pieces on aluminum foil, then ground one at a time in a Hobart commercial meat grinder. After each individual was ground, tissue was mixed well using a stainless steel bowl and spoon. A 50 g aliquot from each specimen was combined to form the composite samples. The combined tissue was then passed twice more through the grinder and thoroughly mixed after each pass.

Composites of Plante Ferry and Lake Spokane suckers consisted of ten specimens each, and composites of Stateline and Ninemile suckers were made from seven specimens each. Homogenized tissue was placed in an appropriate sample container and returned to -20°C until analysis.

Fillet

Rainbow trout fillets were prepared by removing specimens from the freezer and allowing them to partially thaw. Scales and otoliths were removed and mounted or stored for subsequent aging according to WDFW protocols. Specimens were scaled, rinsed with deionized water, and sex was determined by visual inspection of gonads.

Plante Ferry rainbow trout were prepared as ten-fish composite samples, grouped by sex. Ninemile rainbow trout were analyzed individually. Tissue was prepared by removing a skin-on fillet from one side of the fish while on aluminum foil. Composite samples were formed in the same manner as described for whole body samples except that a Kitchen Aid® food processor was used to homogenize tissue rather than a Hobart grinder. Homogenized tissue was placed in an appropriate sample container and returned to -20°C until analysis.

Gut Contents

Gut contents were obtained from suckers other than those used for whole body analysis and from rainbow trout used for fillet samples. Thawed specimens were opened, and the entire gastrointestinal tract was removed, rinsed with deionized water, gently patted dry with a paper towel, and the contents of the stomach was extruded into a pre-cleaned glass jar. In some cases,

rainbow trout stomach contents could only be obtained by slicing open the stomach wall and removing the contents. For suckers, the gut did not have distinctive anatomical components (stomach, intestine), were extremely long (approximately 3 m), and narrow. Therefore, contents from the upper half of the gut were removed for analysis.

Once removed, gut contents were weighed and visual observations were made. Approximately one-half of the rainbow trout had large masses of filamentous plant material in the stomach. In these cases, bugs, mucous bolus, or other food-like material was extracted, and plant material was discarded. Entire gut contents from each specimen were combined for a composite sample, since total mass of material was small and near the minimum amount of material required for analysis. Several grams of material from each species were placed in 20% formalin for subsequent stereoscopic evaluation. The remainder of the collected material was frozen at -20°C until analysis.

Crayfish Tail Muscle

Crayfish (*Pacifastacus leniusculus*) collected from Upriver Dam were allowed to partially thaw. Sex was determined and the entire tail muscle (4-5 g) was removed from the exoskeleton. All tissue from the four specimens obtained were placed together in a pre-cleaned jar, finely chopped and mixed using a clean scalpel, and frozen at -20°C until analysis.

Equipment Cleaning

Prior to sampling, all sampling implements and equipment were cleaned by sequentially:

1. Washing in Liquinox detergent and hot tap water.
2. Rinsing with hot tap water.
3. Rinsing with deionized water.
4. Rinsing with pesticide grade acetone.
5. Air-drying.
6. Rinsing with pesticide grade hexane.
7. Air drying.

After drying, equipment was wrapped in aluminum foil (dull side in) until used in the field. Sampling equipment was dedicated to each station or each sample. Fish processing and tissue homogenization equipment was cleaned between each sample using the described procedure. Persons preparing tissue samples wore non-talc polyethylene or nitrile gloves and worked on aluminum foil. Gloves and foil were changed between samples.

All sample containers were pre-cleaned according to EPA (1990) quality assurance/quality control specification. Samples for PCB analysis were placed in glass jars with Teflon-lined lids. All samples were cooled on ice immediately after collection and transported under chain-of-custody protocols.

Appendix G: Results on Quality Control Samples for 2003-2005

Results of quality control samples analyzed to estimate precision and accuracy are shown in Tables G-1- G-3. Laboratory duplicate analysis of PCB congeners and Aroclors show generally good precision, with relative percent differences (RPDs), the difference as a percentage of the mean, less than 20% when detected.

Equation:
$$RPD = \left(\frac{\text{difference of 2 results}}{\text{mean}} \right) \times 100$$

Table G-1. Precision of Laboratory Duplicates (Mean RPD of Individual PCB Congeners or Aroclors*).

Station	Sample type	Sample number	RPD
Harvard	Surface water	3438100	ND
LIBLAKE	Water (effluent)	4064113	ND
Litlfls	Sediment	3454113	19%
LONGUP2 *		4268384	8%
Spokane-F	Tissue fillet	03084282	5%

ND: not detected at the reporting limit.

Precision of field replicates, which integrates environmental, sampling, and laboratory variability, is shown in Table G-2. Results show that there is substantial variability in SPMD results (average RPD of 28%). Other matrices show lower variability and can be largely accounted for by variation in laboratory analysis.

Table G-2. Precision of Field Replicates (Mean RPD of Individual PCB Congeners).

Station	Sample type	Sample number	Replicate sample number	RPD
Upriver Dam	SPMD	3474156	3474157	9%
		4194131	4194132	55%
UPRIVER BOT		4208136	4208137	20%
LitlSpokR		3474162	3474163	26%
LitlSpokBr		4194136	4194137	25%
		4208140	4208141	35%
SPOKWWTP	Water (effluent)	4188204	4188206	6%
KaiserEff		4064105	4064106	ND
NINEMILE-F	Tissue fillet	4324447	4324448	8%
Spokane-F		3084282	3084308	20%
LongLkLow	Sediment	3454112	3454114	20%

ND: not detected at the reporting limit.

Replicate samples for conventional parameters showed little variation in most cases (Table G-3). Instances of high RPD results were due to small absolute differences at low concentrations which have the effect of amplifying RPDs.

Table G-3. Precision of Field Replicates for Conventional Analytes.

Station	Sample type	Parameter	Sample number	Replicate sample number	RPD
Ninemile 1	Surface water	TOC DOC TSS	4058115	4058114	0% 17% 0%
PLANTEFRY		TOC DOC TSS	3448102	3448101	0% 0% 100%
Upriver Dam		TOC DOC TSS	4208136	4208135	0% 10% 0%
Harvard		TOC TSS	3438103	3438102	9% 0%
Upriver Dam		TOC DOC	3408967	3408972	22% 8%
NINEM SPM		TSS	3454107	3454106	0%
Upriver Dam		TOC DOC	4094045	4094044	15% 0%
		TOC DOC TSS	4164043	4164042	12% 18% 0%
		TSS	4188204	4188206	18%
SPOKWWTP		Water (effluent)	TSS	4064105	4064106
KaiserEff					
LongLkLow	Sediment	Grain size TOC % solids	3454112	3454114	8%* 0% 1%
NINEMILE-F	Tissue fillet	% Lipids	4324447	4324448	8%

*Mean RPD of individual size fractions.

Accuracy of the PCB congener data in sediments was assessed through analysis of the National Institute of Standards & Technology (NIST) standard reference material (SRM) 1944 - New York/New Jersey Waterway Sediment. Results are shown for 12 of the 25 PCB congeners for which SRM 1944 is certified; other individual congeners in SRM 1944 match co-eluting congeners reported by Pace and were not compared (Table G-5). Five of the 12 congeners were within the 95% confidence level of the certified values. Other results were 20%-25% below the certified value, suggesting a low bias for PCB congener results in sediments.

Table H-5. Analysis of NIST 1944 Standard Reference Material (New York – New Jersey Waterway Sediment) by Pace Analytical Services, Inc. (ng/g, dw).

Analyte	Certified concentrations*	Pace Result	% Difference from mean
PCB-008	22.3. \pm 2.3.	23.4	5%
PCB-031	78.7. \pm 1.6	77.6	-1%
PCB-052	79.4. \pm 2.0	80.3	1%
PCB-066	71.9 \pm 4.3	57.1	-21%
PCB-095	65.0 \pm 8.9	48.1	-26%
PCB-099	37.5 \pm 2.4	29.7	-21%
PCB-105	24.5 \pm 1.1	23.5	-4%
PCB-118	58.0 \pm 4.3	52.9	-9%
PCB-194	11.2 \pm 1.4	9.35	-17%
PCB-195	3.75 \pm 0.39	3.91	4%
PCB-206	9.21 \pm 0.51	7.09	-23%
PCB-209	6.81 \pm 0.33	5.43	-20%

*Mean and range of 95% confidence levels.

Shading: Outside certified range of values.

Appendix H: Details of Arnot-Gobas Food Web Bioaccumulation Model

Overview of Arnot-Gobas Food Web Bioaccumulation Model

Models to track hydrophobic organic chemicals through the food web have increased in their accuracy and complexity as investigators have built upon previous models to make iterative improvements. One of the most recently available models, the food web bioaccumulation model developed by Arnot and Gobas (2004), was selected for the present study for several reasons:

1. The model was built upon a widely accepted kinetic model developed to predict bioaccumulation of hydrophobic organic compounds in the food web of Lake Ontario and other lakes (Gobas, 1993).
2. The model is programmed in Excel spreadsheets and is simple to use, make adjustments, and perform backward calculations (find values for input parameters needed to derive a defined model output).
3. Validation runs indicated the model could predict PCB concentrations in at least two Spokane River fish species with a fairly high degree of accuracy.

The model accounts for major routes of PCB accumulation through diet and the gills, while depuration occurs through elimination by the gills and feces and by metabolic transformation (Figure H-1). The model also accounts for decreases in contaminant concentration through growth dilution.

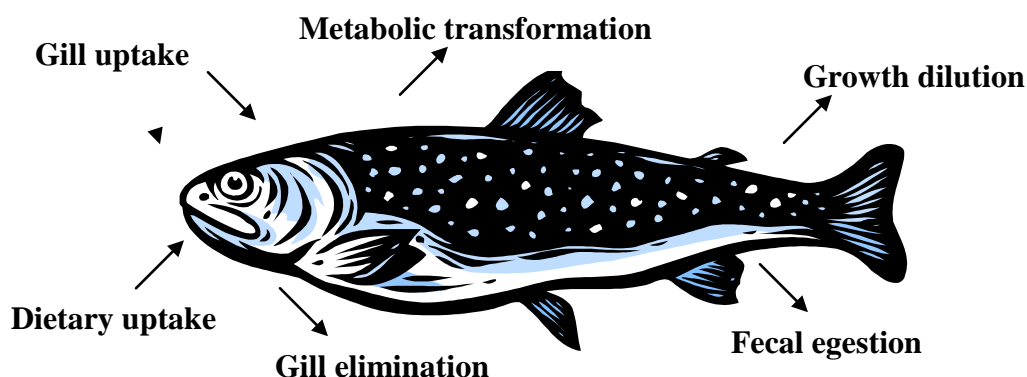


Figure H-1. Conceptual Diagram of the Major Routes of Contaminant Uptake and Depuration (Adapted from Arnot and Gobas, 2004).

The basic equation which describes the general model is:

$$dM_B/dt = \left\{ W_B \cdot \left(k_1 \cdot [m_o \cdot \Phi \cdot C_{wT,0} + m_p \cdot C_{wD,S}] + K_D \cdot \sum (P_i \cdot C_{d,i}) \right) \right\} - (k_2 + k_E + k_M) \cdot M_B$$

Where:

M_B = mass of the chemical in the organism (g)

t = time (d)

dM_B/dt = net flux of chemical in the organism at any point in time

W_B = weight of the organism at t (kg)

k_1 = clearance rate constant for the chemical uptake via gills and skin (L/kg • d)

M_o = fraction of respiratory ventilation in overlying water

M_p = fraction of respiratory ventilation in pore water

Φ = fraction of total chemical concentration that is freely dissolved in overlying water

$C_{wT,0}$ = total chemical concentration in water above sediments (g/L)

$C_{wD,S}$ = chemical concentration freely dissolved in pore water (g/L)

K_D = clearance rate constant for the chemical uptake via diet (kg/kg • d)

P_i = fraction of diet consisting of prey item i

$C_{d,i}$ = chemical concentration in prey item i (g/kg)

k_2 = rate constant for the chemical elimination via gills and skin (d⁻¹)

k_E = rate constant for the chemical elimination via fecal egestion (d⁻¹)

k_M = rate constant for metabolic transformation of the chemical (d⁻¹)

The general equation can be simplified by assuming steady-state conditions (i.e., $dM_B/dt = 0$), which results in a re-expression of the equation to:

$$C_B = \left\{ k_1 \cdot \left(m_o \cdot \Phi \cdot C_{wT,0} + m_p \cdot C_{wD,S} \right) + K_D \cdot \sum (P_i \cdot C_{d,i}) \right\} / (k_2 + k_E + k_M + k_G)$$

Where:

C_B = chemical concentration in the organism (M_B/W_B)

The steady-state assumption necessitates a growth dilution term (k_G) which can be represented by a constant fraction of the organism's body weight. The reader is referred to Arnot and Gobas (2004) for detailed explanations of the sub-models used to derive all of the terms in the general equation. Assumptions and input parameters used to apply the model to the Spokane River are discussed below. All other environmental characteristics were those used for Lake Erie modeling and were supplied by J. Arnot.

Environmental characteristics

Environmental characteristic input parameters for the Spokane River model included mean annual water temperature, DOC, TSS, particulate organic carbon (POC), and sediment TOC. Table H-1 shows the values used. Mean annual temperatures, DOC, and TSS were mean values of the reaches modeled from data collected during SPMD deployment and recovery. One-half the detection limits were used for non-detects. Since January-February data for temperature

were lost at Ninemile, the Monroe-Ninemile model was run using mean temperature data only from Monroe St. POC was calculated as the fraction organic carbon (f_{oc}) in suspended particulate matter (0.15, see Eq. 3) multiplied by TSS.

Table H-1. Input Parameters for the Arnot-Gobas Food Web Bioaccumulation Model.

	Reach				
	Stateline-Upriver	Monroe-Ninemile	Long Lake	Little Falls	Spokane Arm
Water					
Mean annual water temperature (°C)	9.2	8.9	10.0	10.0	10.0
DOC (mg/L)	1.2	1.0	1.1	1.1	1.1
TSS (mg/L)	1.6	2. 2	2.8	2.8	2.8
Particulate organic carbon (mg/L)	0.24	0.33	0.42	0.42	0.42
Sediment					
TOC (%)	2.0	1.6	2.9	0.6	1.7
Zooplankton					
Diet	100% phytoplankton				
Benthic Species					
Diet	50% phytoplankton, 50% sediment				
Rainbow Trout					
Weight (kg)	0.5				
Lipid (%)	5.6				
Diet	50% zooplankton, 12.5% each may-fly larvae, chironomid larvae, <i>Gammarus</i> , crayfish				
Sucker					
Weight (kg)	0.918				
Lipid (%)	3.8				
Diet	33% phytoplankton, 33% chironomids, 34% sediment		50% chironomids, 50% sediment		
Chemical (Total PCBs)					
Log K _{ow}	6.4				
Henry's Law Constant (Pa. m ³ /mol)	3.9				

OC = organic carbon.

Pa = Pascals

Sediment TOC concentrations were more difficult to estimate due to lack of depositional material in the upstream reaches. For the Stateline-Upriver model run, the TOC was the mean of five sediments from RM 81.5-94.8 analyzed by Ecology (1994). Sediments from the Upriver Dam PCB "hot spot" were not used to derive this value. For the Monroe-Ninemile model run, the TOC value was the mean TOC of five Monroe St. (RM 74.9-78.7) sediments collected during 1994 averaged with a single Ninemile sediment collected during 1993 (Ecology, 1994).

Species characteristics

Fish species used for target PCB concentrations were rainbow trout and suckers. The model has output parameters built in for rainbow trout. The sucker species built into the model is white sucker (*Catostomus commersoni*). This species has similar habits and foraging characteristics as

largescale and bridgelip suckers, and may even interbreed with largescale suckers where their ranges overlap (Wydoski and Whitney, 1979), and was therefore deemed a suitable substitute.

The model also allows for yellow perch, smallmouth bass, and largemouth bass as target endpoints (criteria). These species are found in Lake Spokane and the Spokane Arm, with limited populations of smallmouth bass in upstream reaches. However, these species were not selected to establish critical PCB concentrations because they generally have much lower PCB concentrations than lipid-rich species such as trout and sucker (e.g. Ecology, 1995; Jack and Roose, 2002). For these species, the target tissue concentration of 0.1 ng/g would be achieved with much higher water and sediment PCB levels.

Rainbow trout lipid content used in Table H-1 was the average of rainbow trout analyzed whole from four Spokane River locations. Weight was an approximation of present and historical Spokane River rainbow trout collected for analysis. For largescale suckers, lipid fraction in Table H-1 was an average of whole bodies from all available Spokane River samples, historic and present. Weight was the average of all suckers analyzed whole for the present study.

Diet of target fish species in Table H-1 was based on observations of gut contents. Diet composition of fish prey items (zooplankton and benthic species) was based on likelihood rather than site-specific observations.

Whole body to fillet conversion

The model produces a whole organism output for PCB concentrations in fish, which assumes that the chemical is distributed homogeneously among tissues of an organism. This limitation of the model may be an over-simplification when applied to complex organisms such as fish. To achieve the target concentration in fillet tissue, a conversion factor of 1.47 was applied based on the work of Amrhein et al. (1999). Limited data on paired whole fish-fillet data from the Spokane River (Johnson, 2000) yielded a conversion factor of 1.18 for rainbow trout and 2.73 for largescale suckers. This indicates that the water and sediment PCB concentrations used in the model along with the published conversion factor may be conservative for predicting target concentrations in suckers, while those used to predict rainbow trout targets may contain a slightly high bias.

Chemical characteristics

Total PCB was analyzed as the chemical of interest in the model to provide a simplified method of calculating PCB endpoints. The log K_{ow} and Henry's Law constant for total PCB used for the model were the same as those used to translate SPMD concentrations to water concentrations (Table H-1). For SPMDs, these parameters yield values similar to total PCBs calculated by summing individual congeners separately.

Validation and sensitivity

Prior to use, the model was validated using input parameters representative of the Spokane River and reach-specific fish weight and lipid data from recent sampling. Predicted and observed tissue concentrations were similar (Table H-2).

Table H-2. PCB Concentrations in Fish Tissue Predicted Using the Arnot-Gobas Food Web Bioaccumulation Model vs. Observed PCB Concentrations.

	Reach				
	Stateline-Upriver	Monroe-Ninemile	Lake Spokane	Little Falls	Spokane Arm
Measured PCB concentrations in water and sediment					
Dissolved total PCB conc. in water (pg/l)	83	222	332	na	na
total PCB conc. in sediment (ng/g dw)	54	78	33	1.9	10
Total PCB concentrations in whole rainbow trout (ng/g ww)					
Predicted	87	31**	55	--	--
Observed*	51	40**	na	na	na
Total PCB concentrations in whole suckers (ng/g ww)					
Predicted	110	26**	98	--	--
Observed*	99	29**	224	na	na

*PCB concentrations in fillet converted to whole fish by multiplying by 1.47.

**Ninemile only. Recent tissue data not available for Monroe St.

na: not available.

The model was not calibrated by adjusting the algorithms to match predicted and observed results. The decision to apply this model was made only after sampling had been completed. However, the necessary input parameters were easily obtained from current or historical data, and default values for physical, chemical, and species characteristics – originally used to model PCBs in the Lake Ontario food web – are applicable to the Spokane River.

A cursory assessment of model sensitivity was done by inserting ranges of values for the input parameters discussed in previous sections. The model is somewhat sensitive to changes in POC, sediment TOC, percent lipid in target fish, and prey composition for target fish. A 50% change in these model parameters results in an approximate 15% change in the target fish PCB concentrations when other model parameters are held at values typical for the Spokane River.

The model is particularly sensitive to $\log K_{ow}$ values, which can be expected due to the $\log K_{ow}$ as one of the most important factors driving the partitioning of PCBs between water and lipid soluble compartments. The response to changes in $\log K_{ow}$ is an approximate 10% decrease in target fish PCB concentrations with each 0.1 decrease in $\log K_{ow}$ around the value used for the Spokane River ($\log K_{ow} = 6.4$). Increases of 0.1 in $\log K_{ow}$ result in approximately 10% increases in fish PCB concentrations. Of course, these responses are not linear, and the limited information provided here cannot be used to calculate target fish PCB concentrations, but they offer a glimpse at how the model output responds to certain input parameters.

Appendix I: Glossary Acronyms, Symbols, and Units

Ambient: Surrounding environmental condition (for example, surrounding air temperature).

Benthic: Bottom-dwelling organisms.

Best Management Practices (BMPs): Physical, structural, and/or operational practices that, when used singularly or in combination, prevent or reduce pollutant discharges.

Clean Water Act: Federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act identifies water quality impaired waterbodies.

Composite sample: A representative sample created by the homogenization of multiple fish.

Congener: In chemistry, congeners are related chemicals. For example, polychlorinated biphenyls (PCBs) are a group of 209 related chemicals that are called congeners.

Designated uses: Those uses specified in Chapter 173-201A WAC (Water Quality Standards for Surface Waters of the State of Washington) for each waterbody or segment, regardless of whether or not the uses are currently attained.

Discharge: The rate of streamflow at a given instant in terms of volume per unit of time, typically cubic feet per second.

Effluent: An outflowing of water from a natural body of water or from a man-made structure. For example, the treated outflow from a sewage treatment system.

Exceeded criteria: Did not meet criteria.

Harmonic mean flow: One of several methods of calculating an average rate of flow. The harmonic mean is defined as $Q_h = n/\Sigma(1/Q_i)$ where n is the number of recorded flows Q_i . The harmonic mean is never larger than the geometric mean or the arithmetic mean.

Grab: A discrete sample from a single point in the water column or sediment surface.

Homologue: A chemical compound from a series of compounds that differs only in the number of repeated structural units.

Legacy pesticides: Banned pesticides no longer used but that persist in the environment.

National Pollutant Discharge Elimination System (NPDES): National program for issuing, modifying, revoking and reissuing, terminating, monitoring and enforcing permits, and imposing and enforcing pretreatment requirements under the Clean Water Act. The NPDES program regulates discharges from wastewater treatment plants, large factories, and other facilities that use, process, and discharge water back into lakes, streams, rivers, bays, and oceans.

Parameters: Water quality constituent being measured (analyte). A physical, chemical, or biological property whose values determine environmental characteristics or behavior.

Point source: Sources of pollution that discharge at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites that clear more than 5 acres of land.

Pollution: Such contamination, or other alteration of the physical, chemical, or biological properties, of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state. This definition assumes that these changes will, or are likely to, create a nuisance or render such waters harmful, detrimental, or injurious to (1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

Reach: A specific portion or segment of a stream.

Sediment: Solid fragmented material (soil and organic matter) that is transported and deposited by water and covered with water (example, river or lake bottom).

Stormwater: The portion of precipitation that does not naturally percolate into the ground or evaporate but instead runs off roads, pavement, and roofs during rainfall or snow melt. Stormwater can also come from hard or saturated grass surfaces such as lawns, pastures, playfields, and from gravel roads and parking lots.

Surface waters of the state: Lakes, rivers, ponds, streams, inland waters, salt waters, wetlands, and all other surface waters and water courses within the jurisdiction of Washington State.

Suspended particulate matter (SPM): Particulates suspended in the water column.

Total Maximum Daily Load (TMDL): A distribution of a substance in a waterbody designed to protect it from exceeding water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a Margin of Safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

Total suspended solids (TSS): The suspended particulate matter in a water sample as retained by a filter.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

303(d) list: Section 303(d) of the federal Clean Water Act requires Washington State periodically to prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality limited estuaries, lakes, and streams that fall short of state surface water quality standards, and are not expected to improve within the next two years.

Acronyms, Symbols, and Units of Measurement

303(d):	Section 303(d) of the federal Clean Water Act
BAF:	bioaccumulation factor
BCF:	bioconcentration factor
BSAF:	biota-sediment accumulation factor
BW:	body weight
CFR:	Code of Federal Regulations
CSO:	combined sewer overflow
DOC:	dissolved organic carbon
dw:	dry weight
Ecology:	Washington State Department of Ecology
EIM:	Environmental Information Management (Ecology database accessible through internet)
EPA:	U.S. Environmental Protection Agency
FS:	feasibility study
GC/ECD:	gas chromatography/electron capture detection
GC/MS:	gas chromatography/mass spectrometry
MTCA:	Model Toxics Control Act
N:	number of samples
NIST:	National Institute of Standards and Technology
NPDES:	National Pollutant Discharge Elimination System
NTR:	National Toxics Rule
PCB:	polychlorinated biphenyl
RF:	risk factor
RI:	remedial investigation
RM:	river mile
RPD:	relative percent difference
SPM:	suspended particulate matter
SPMD:	semi-permeable membrane device
SRM:	standard reference material
SV:	screening value
TMDL:	Total Maximum Daily Load
Total PCB:	the sum of PCB congeners or Aroclors (also t-PCB)
TOC:	total organic carbon
TSS:	total suspended solids
UWP:	Spokane River Urban Waters Program
USGS:	U.S. Geological Survey
WAC:	Washington Administrative Code
WC:	water consumption
WDFW:	Washington Department of Fish and Wildlife
WDOH:	Washington State Department of Health
WQS:	water quality standard(s)
WRIA:	Water Resource Inventory Area

WSTMP:	Washington State Toxics Monitoring Program
ww:	wet weight
WWTP:	waste water treatment plant
C_d :	concentration in the dissolved phase
C_s :	concentration in sediment or solids
C_t :	concentration in tissue
C_w :	concentration in whole water
f_{oc} :	fraction of organic carbon
f_s :	fraction of solid in water
K_{oc} :	sediment-water partition coefficient normalized for organic carbon
K_{ow} :	octanol-water partitioning coefficient
Q:	discharge
q_1^* :	cancer slope factor
Pb:	lead
g:	gallon
cm:	centimeter
kg/day:	kilograms per day
L/kg:	liters per kilogram
MGD:	million gallons per day
mg/day:	milligrams per day
mg/L:	milligrams per liter (parts per million)
ML:	megaliter (one million liters)
mm:	millimeter
ng/g:	nanograms per gram (parts per billion)
ng/L:	nanograms per liter (parts per trillion)
pg/g:	picograms per gram (parts per trillion)
pg/l:	picograms per liter (parts per quadrillion)
Pa m ³ /mol:	Pascals cubic meter/mole